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ON THE EVALUATION OF NUTRIENT POOLS OF FOREST SOILS

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Abstract—The standard method of assessing the available portion of the nutrient reservoir of a forest soil is to use a neutral salt solution, such as NH_4OAc, to extract the exchangeable plus dissolved ions, which are analyzed and considered available. This approach, designed for evaluating nutrients available for the short growth term of agricultural crops, is inadequate for assessing the nutrient pool of forests where tree growth term may reach 100 yr or more.

Soil nutrient reservoirs were evaluated in two forest soils for K, Na, Ca, Mg and Fe, using an approach based on continuous extraction of the elements and kinetic analyses of the extraction rate curves. The analyses of the curves indicate that K, Na, Ca and Fe are each released at four separate constant rates, and Mg is released at three separate constant rates. By analogy with similar kinetic studies done on monomineralic layer silicate samples, each separate extraction rate is thought to correspond to a single type of bond site in the soil. Higher extraction rates indicate greater ease of removal and are interpreted as indicating a higher degree of availability relative to the extractant.

The available K reserves of the Everett soil evaluated by standard methods, compared with annual net K uptake rates of its forest system, indicates growth limiting K deficiency in 12–17 yr. K availability assessed by kinetic analyses indicates about 100 yr supply of K is available.

INTRODUCTION

Significant increases in rates of nutrient losses from forest soils result from man-caused perturbations of forest watersheds. Some common timber harvest methods, including clearcutting, are among the perturbations known to cause increased nutrient loss rates (Likens *et al.*, 1970; Bateridge and Thompson, in preparation; Pierce *et al.*, 1972; Gessel and Cole, 1965; Frederickson, 1971; Brown *et al.*, 1973). These relationships indicate the importance of detailed studies of the effects of such nutrient losses on the total nutrient pools of forest soils, and hence, of the need for methods which characterize in detail the nutrient pools of such soils.

Standard methods of assessing available nutrients in forest soils use techniques developed for short-term (i.e. one growing season) agricultural crop systems. Many variations are used, but basically the exchangeable plus dissolved ions are extracted using a neutral salt solution such as 1 N NH_4OAc, and are analyzed and considered as 'available'. It has long been known, however, that nutrients are available to plants in larger amounts than those measured by determinations of exchangeable plus dissolved ions, and that these nutrients may be considered a part of the available nutrient reservoir, but are more firmly bound than exchangeable ions. Methods of measuring such less available ions are usually quite specialized, involving a single extraction with an agent somewhat more vigorous than NH_4OAc. The resulting analysis gives a value corresponding to the total quantity of ions which can be removed by the particular extractant employed during the time interval that the soil was exposed to the extractant. Such analyses do not provide a good characterization of the nature of the total nutrient pool of a soil, and it appears that there is not a generally used method for such a characterization.

In forest soils, nutrients more firmly bound than exchangeable ions, thus available to plants at slower rates, assume major importance in relation to the longevity and growth rates of the plant species involved. A method developed by us to quantify these additional sources of nutrients, and the general nature of the results, may be of interest to others working in fields related to forest soils.

The method consists of a leaching process in which the soil sample is exposed to a solution which progressively extracts ions from the soil. Thus far, we have used only dilute acids (e.g. 0.5 N HCl), for the leaching solution, but other solutions could be used which more closely approximate those found in natural systems. The solution is withdrawn at timed intervals and analyzed for the nutrients of interest. The least strongly held fractions of any nutrient are removed at the fastest rates. By plotting the results of the analyses against the time the sample was exposed to the leaching solution in a standard reaction rate curve, and carrying out a simple analysis of the curve, it is possible to evaluate quantitatively the distribution of the nutrients between various rates of extraction, and hence to arrive at interpretations of relative ease of removal (and by inference, 'availability') of the various amounts of the nutrient.

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SAMPLES

A careful study of nutrient cycling by Cole *et al.* (1967) in a 40-yr-old even-age stand of Douglas fir at the Cedar River Research Station about 40 miles southeast of Seattle, Washington, allowed calculation of the net annual potassium uptake. A comparison of this uptake value with the 'available' potassium determined by standard cation exchange determinations indicated that the potassium supply in the soil (Everett series) would be exhausted within a minimum of 12.5, and a maximum of 17 yr. Samples of the Everett soil were collected from this experimental site for analysis in an effort to characterize the total K pool and further investigate the possibility of K exhaustion. This soil is a member of the loamy-skeletal, mixed, mesic family of Typic Haplorthods. Everett soils are formed on glacial outwash terraces at elevations ranging from sea level to 500 ft. Parent materials are derived from granite, quartzite, shale, sandstone, schists, basalt and andesite. A second set of soil samples was taken from the H. J. Andrews Experimental Forest about 60 miles south of Corvallis, OR. This soil is of the Frissell series, and is tentatively classified as a member of the loamy-skeletal, mixed, mesic family of Typic Dystrochrepts. Parent materials are alluvium–colluvium derived from breccia, tuff and andesite.

ANALYTICAL METHODS

1. *Analyses of total* K, Na, Mg, Ca *and* Fe *in the soils*

Total K, Na, Mg, Ca and Fe were determined by hydrofluoric acid digestion; following dilution, the cations were analyzed by the same techniques described in the next section.

2. *Progressive leaching technique*

The apparatus and procedure has been described in detail elsewhere (Mandzak *et al.*, 1976). It essentially consists of a temperature controlled, glass chromatography column 27 cm long and 48 mm o.d. in which a weighed soil sample of approximately 10 g was settled upon a specially prepared filtration bed. Fifty ml of a prewarmed extractant consisting of 0.5 N HCl was added to the column at the beginning of the series of extractions, and then the extractant was withdrawn at timed intervals by gentle vacuum and a flush of an additional 30 ml of 0.5 N HCl also pre-

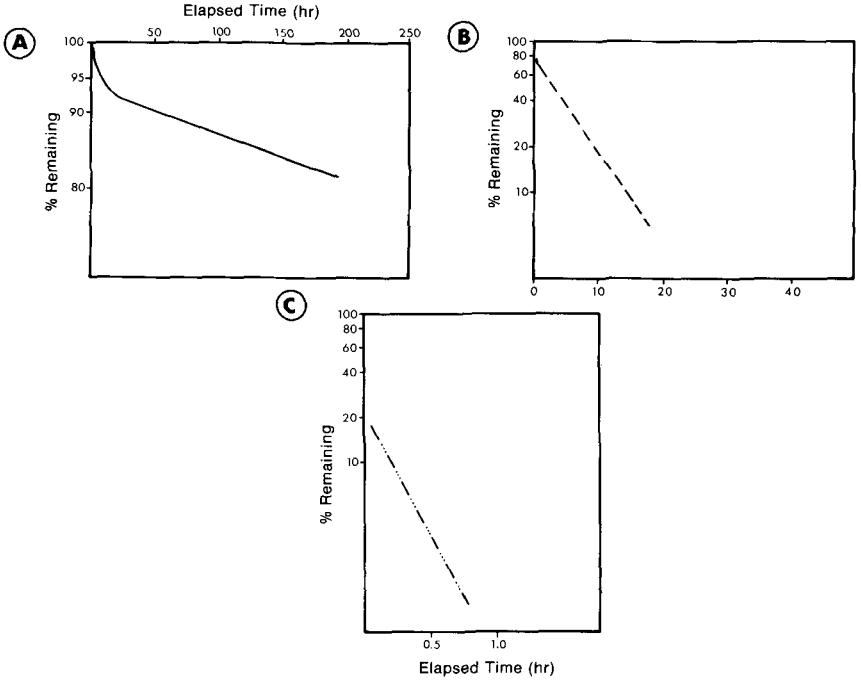


Figure 1. Extraction of K from Everett soil at 80°C. (A) The extraction curve obtained by analysis of 47 sequential soil extractions with 0.5 N HCl. The Everett soil contains 0.74% K (Table 1). Extrapolation of the linear portion of the extraction curve to 93.4% at time zero indicates that 93.4% of the K is contained in the most firmly bound category which we interpret to be structural sites in unweathered or primary minerals. (B) The first deconvolution of (A) obtained by subtracting the extrapolated linear portion from the curved portion of that line. This extrapolation to 73% indicates that 4.83% of the K is contained in the next most firmly bound site (100–93.4%) (73%). (C) The second deconvolution obtained by subtraction of the extrapolated linear portion of (B) from its curved portion. This extrapolation to 17% at time zero indicates that 0.30% of the soil's K is in the second least firmly bound site (100–98.23%) (17%). The remaining 1.48% of the soil's K was extracted at the most rapid rate and thus was least firmly bound. This value compares with that obtained by 1 N NH_4OAc extraction (Table 1).

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warmed to the temperature selected for that determination. The extraction interval was established by allowing sufficient time to yield an elemental concentration high enough for accurate analysis. As many as five extractions were made during the first hour, but near the end of a series of about 200 hr of elapsed time, extractions were made only once or twice daily. Approximately 50 extractions were made of each sample.

In order to prevent the precipitation of the solutes dissolved at the 60 or 80° extraction temperatures upon cooling to room temperature, the first five 80-ml extracts (which contained the highest concentration of dissolved solutes) were immediately diluted to nearly 250 ml and the rest to nearly 100 ml with water and a solution of lanthanum chloride in 0.5 N HCl designed to give a final concentration of 1000 ppm lanthanum. The purpose of the lanthanum was to prevent interference by phosphate and aluminate ions with Ca and Mg determinations. The final dilutions were made after the solution reached room temperature.

Analyses for Ca, Mg and Fe were made within 24 hr of extraction to nullify the effects of precipitation or reaction with the sample vials. K and Na were analyzed by flame emission spectrophotometry and Ca, Mg and Fe were analyzed by atomic absorption spectrometry.

3. *Treatment of analytical data*

The results of the analyses of the extracting solutions were plotted as in Figure 1 as ln α vs time, where α is the percentage of the nutrient remaining unextracted in the sample (i.e. 100% − % extracted), and time is cumulative hours the soil sample was exposed to the extraction procedure.

Previous studies (Brindley and Youell, 1951; Osthaus, 1954, 1956; Grandquist and Sumner, 1957; Cloos *et al.*, 1961; Ross, 1969; Thompson and Hower, 1973; Thompson and Hower, 1975) have established that acid dissolution of specific ions in layer silicates obeys first order rate laws, when carried out with a large excess of acid. This means that the extraction rate, expressed as the rate of change of concentration of the ion under consideration remaining in the silicate mineral, is constant. When the log of the concentration is plotted against time, a straight line results for a first order reaction. If an ion is bonded in two different structural sites, the ion generally will be removed at two different rates and a plot of log concentration vs time will be the sum of two linear extraction rates and will appear as a curve. When such a curve results, it can be deconvolved (i.e. separated into extraction rates for the ion from each bond site) by subtracting the contribution by the site with the lowest rate and plotting the remainder on another log concentration vs time curve. This is done by extrapolating the linear portion of the curve at long times (where the contribution of the higher rate curve is insignificant) back to zero and subtracting this from the total curve. If more than two extraction rates exist, the process can theoretically be continued to complete deconvolution (Thompson and Hower, 1975). The amount of the ion in each bond site is also given by the deconvolution.

As will be seen in the data which follow in the next section, the Everett and Frissell soils produce extraction results remarkably similar to the results for pure, monomineralic layer silicates, in that the extraction data for the soils yield a few straight lines upon deconvolution, even though the soils contain substantial organic material, and are not monomineralic (Schlicte, 1968). Each straight line produced by deconvolution of the extraction curves for the soil samples indicates a separate constant extraction rate. By analogy with work on pure silicate minerals, each separate constant extraction rate from the soil samples is interpreted as indicating a separate kind of bond site for the ion under consideration. The more rapid extraction rates are interpreted as indicating greater ease of removal of an ion from the soil, and hence, a high degree of 'availability' relative to the extractant.

RESULTS

The results of the extractions for the samples of the Everett and Frissell soils are plotted below for Ca, Mg, Fe, K and Na, in Figures 1 and 2. The relative amount of each ion in each separate bond site in the soils is summarized in Table 1. Determinations of exchangeable K, Na, Ca, Mg, and Fe also are presented in Table 1.

DISCUSSION

It can be seen from Figures 1 and 2 and Table 1 that both the Everett and Frissell soils show four separate constant extraction rates for K, Na, Ca and Fe, and three each for Mg. It also appears that these ions are bonded only in specific sites, and very little, if any, of the elements are held in the soils in sites other than those described by the constant extraction rates.

Analysis of the extraction curves does not lead directly to interpretations of the natures of the specific bond sites for the five elements beyond the implication that the highest extraction rate corresponds to the least firmly bound element, and the lowest rate to the most firmly bound. However, it appears reasonable to suggest that the quantities of elements with the lowest extraction rates are being removed from structural sites in unweathered or primary minerals in the soils, as such sites should hold the elements most firmly. It also seems reasonable to interpret the most rapidly removed portions of each element as being equivalent to the exchangeable quantities determined by standard methods.

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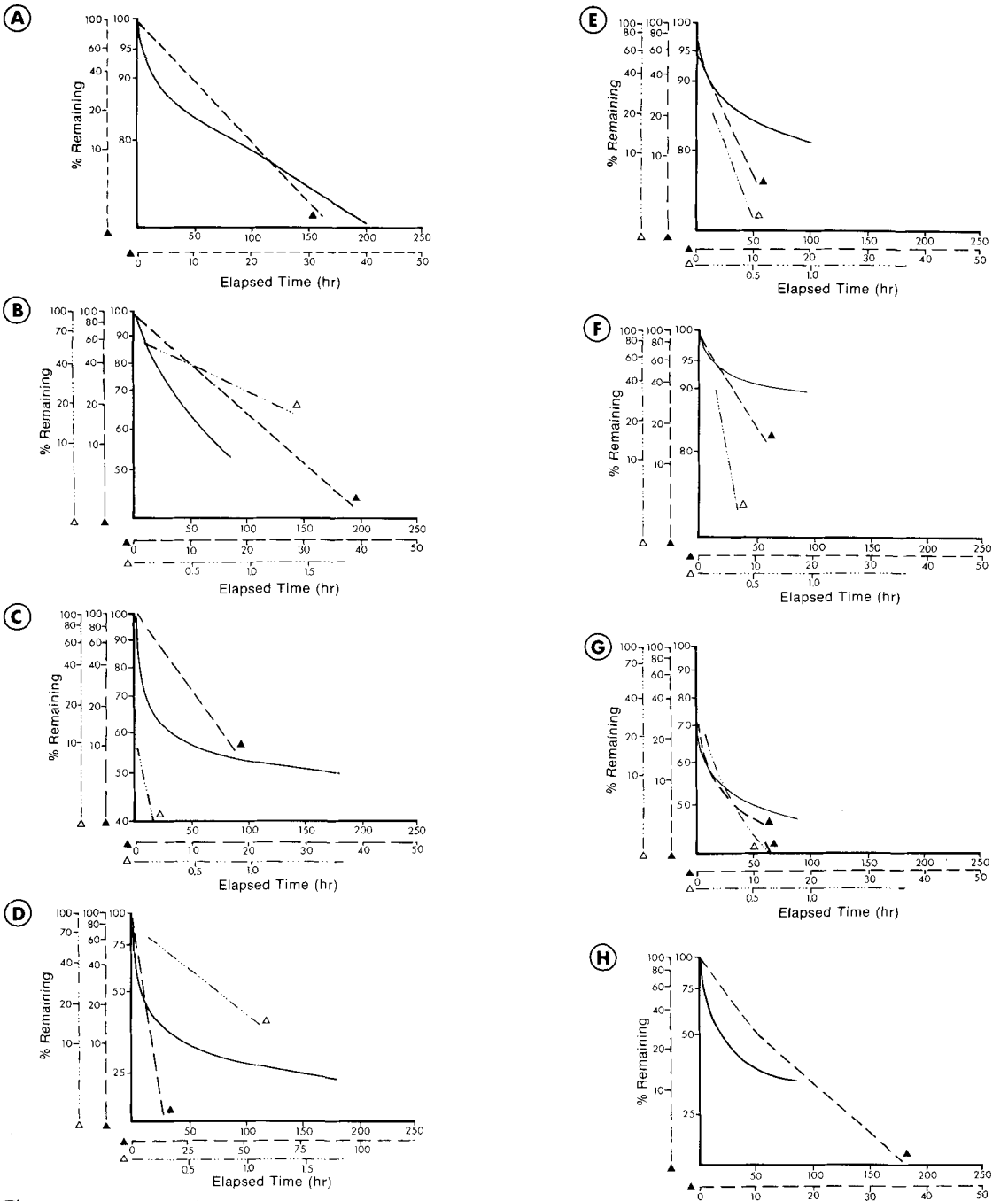


Figure 2. Extractions of elements from Everett and Frissell soils at 80°C. The extraction curves and deconvolutions were obtained by the same methods described in Figure 1 but are combined to conserve space. ——, extraction curve, – – – –▲, first deconvolution, — · · · — · · · △, second deconvolution. There is no second deconvolution for Mg. The relative quantities of each element in each site in the different soils as computed from the intercepts of the extrapolated portions of the curves are shown in Table 1. The curves illustrate that soil nutrients are contained in distinct bond sites which can be characterized by constant extraction rates and which allow quantitative determination. (A), Extraction of Na from Everett soil. (B), Extraction of Ca from Everett soil. (C), Extraction of Mg from Everett soil. (D), Extraction of Fe from Everett soil. (E), Extraction of K from Frissell soil. (F), Extraction of Na from Frissell soil. (G), Extraction of Ca from Frissell soil. (H), Extraction of Mg from Frissell soil. (I), Extraction of Fe from Frissell soil.

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Table 1

	Soil											
	Everett						Frissell					
			% total in each bond site (extraction rate)						% total in each bond site (extraction rate)			
Element	% Weight	% total removed by 1N NH_4OAc	Most rapid 1	2	3	Slowest 4	% Weight	% total removed by 1N NH_4OAc	Most rapid 1	2	3	Slowest 4
K	0.74	1.13	1.48	1.30	4.83	93.4	0.74	3.30	1.14	0.82	8.04	90.0
Na	1.33	3.96	0.31	0.04	4.90	94.7	1.38	2.83	0.21	0.33	2.81	96.7
Ca	0.97	2.36	0.30	1.30	14.5	83.9	0.29	1.47	32.0	4.49	6.43	57.0
Mg	1.20	0.14	1.50	39.0		59.5	0.68	0.17	1.64	51.8		46.5
Fe	4.04	0.003	5.59	14.7	39.0	40.7	7.19	0.002	0.83	14.4	56.0	28.2

Table 2 shows a comparison of exchangeable values for the ions with the values for the most rapidly extracted amounts (site 1) of the ions, expressed as percentage of ion in site 1 divided by exchangeable percentage of the same ion. Given the considerable differences in the extractants used, the exchangeable values for K, Na and Mg are reasonably similar to the site 1 values for the same ions. There are, however, extreme differences for Ca and Fe, which are not understood.

The ion bond sites with extraction rates intermediate between the fastest and slowest rates probably are located in partly weathered mineral fractions and/or in organic fractions of the soils. Work is continuing on characterizing the precise nature of such sites.

If one considers the K in all but the most slowly soluble sites to be available to growing trees in the Everett soil, based on the annual K uptake data of Cole *et al.* (1967), there is between 70 and 100 yr worth of K available for tree growth at the Cedar River Research Station. This implies that the forest will not suffer a growth-limiting K deficiency as implied by measurements of exchangeable K.

The implications of the results of this study for forest management are important. When a forest is harvested using certain kinds of practices, major acceleration of nutrient losses can occur. The bulk of this nutrient loss almost certainly occurs by flushing of nutrients from the soil solution and from the exchangeable ion sites in the soils, as well as from erosional losses of soil components. The nutrient supply for the re-establishment of the forest will be accessible, however, either directly from one or both of the 'slower' sites defined in this study, or via the replenishment of the exchangeable portion of the nutrient pool from these 'slower' sites. However, if these 'slower' sites are themselves depleted by repeated major nutrient loss episodes, there may be a very real possibility of growth-limiting nutrient deficiencies after a few such episodes, depending, of course, on weathering rates. A danger lies in the possibility of being misled, by the observation of one or two successful reforestations, into believing that weathering of primary minerals proceeds at a rate adequate to accommodate an indefinite number of major nutrient loss episodes. In fact, what one may be observing is the depletion of the limited available nutrient pool from the sites described by the intermediate extraction rates, at a rate far greater than nutrients are replenished in these sites by weathering of primary minerals. We suggest that, in order to make realistic calculations regarding the rate of nutrient loss which a forest soil can sustain without suffering growth-limiting nutrient depletions, it is necessary to know much more than is presently known about weathering rates of primary minerals in various environments, and about nutrient loss rates associated with timber harvest practices. It can be misleading to rely on observations of a few successful reforestations for a conclusion that forest soils can indefinitely sustain repeated major nutrient loss episodes without artificial replenishment (e.g. fertilization).

Table 2

	$\frac{\%\text{ in Site 1}}{\%\text{ extracted by } NH_4OAc}$	
	Everett	Frissell
K	0.8	2.9
Na	0.5	0.8
Ca	13.0	0.1
Mg	1.7	0.9
Fe	0.0005	0.0002

SUMMARY

1. Progressive extraction analyses of the nutrient pools of the Everett and Frissell soils show, by analogy with the extraction data from layer silicates, that K, Na, Ca and Fe are held in four separate bond sites each, and Mg is held in three separate bond sites, in both soils. The bond sites are well characterized by constant extraction rates for each cation. Such analyses allow quantitative determination of the distribution of the cations among the bond sites.

2. Because the major growth period of a tree comprises several decades rather than a few months as in annual crops, cation exchange-type evaluations of forest soil nutrient pools are inadequate. An approach to forest soil nutrient evaluation based on progressive extraction analyses allows a more complete characterization of a forest soil nutrient pool.

3. Assessment of forest practices which produce accelerated rates of nutrient loss from forest soils must take into account nutrient distribution between

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the various bond sites, as defined by constant extractive rates, in determining the real effects on the soil nutrient pool.

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