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Cation Exchange Properties of Forest Litter as Influenced by Vegetation Type and Decomposition

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Susan Ann Warner

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Decomposition of forest litter is a complex process involving interactions between physical, chemical and biological factors. As litter decomposes it is chemically altered. Cation exchange capacities of litter represent a means of characterizing the number of hydrophilic acid groups. Some kind of soil-root ion exchange mechanisms are utilized by the plant for uptake of most nutrients.

Cation exchange capacities were determined by ammonium saturation and subsequent Kjeldahl distillation. Solvent extractions of some litters were made with water at three different temperatures, and with isopropanol, ethanol, acetone, water, NaOH, and HCL. The extracted litter was used for CEC determinations.

A variety of forest floor materials from different forest types in Eastern North America and Oregon were used in this study. L, F, and H layers were used to determine the effect of decomposition on CEC. Significantly increased CEC magnitudes with increased decomposition was shown for the Oregon samples. Eastern forests also showed increased CEC's with increased decomposition except where high ash contents of an H layer resulted in lower CEC values.

Litter samples from the various Oregon forest types showed significant differences in CEC's between vegetation types. Litters from more productive timber sites had greater CEC values for L and F layers than litter from less productive sites.

Organic solvents extracted significantly less material from litter than inorganic solvents. Hot water extracted more material from litter than cooler temperature water. CEC's of litter extracted with organic solvents were lower than CEC's of litter extracted with inorganic solvents.

Litter collected from streams showed CEC values for bark to be highest and twigs to be lowest. Litter that was more highly decomposed by stream activity had higher CEC's than less decomposed samples.

Pre- and post-logging samples that represented combined L + F + H layers did not show significant differences in CEC values between vegetation types. APPROVED:

Professor Forest Soils in charge of major

Head of Department of Soil Science

Dean of Graduate School

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INTRODUCTION

Forest floor litter is probably the most active, dynamic phase in the forest ecosystem. It is subject to intense microbial activity, large scale biological, chemical and physical alterations and extreme climatic fluctuations.

The forest floor layers are of great importance to several aspects of forest management. Regeneration of one tree species may be favored over another by eliminating or disturbing the forest floor. Differences in soil humus types have been used to predict site quality for timber productivity (Ovington, 1954).

Decomposition of forest litter is a complex, mutable process involving interactions between physical, chemical and biological factors. Cation exchange capacities represent a means of characterizing the number of hydrophilic acid groups. Cation exchange capacities have been suggested (Kyuma and Kawaguchi, 1966) as giving an indication of the stage of decomposition.

Objectives

The three major objectives in this study were to determine the effect of: 1) litter decomposition on cation exchange capacity of the forest floor; 2) vegetation on cation exchange of forest litter; 3) several chemical

capacity of litter.

REVIEW OF LITERATURE

The chemistry of the forest floor plays an important role in the nutrient cycles of a forest. These cycles are dependent upon several factors, including the type of vegetation returning organic debris to the forest floor and the conditions under which that debris is decomposed.

Leaves and other litter accumulate on the forest floor and are subjected to decomposition by soil macro- and microorganisms. Nutrients are gradually liberated or altered to forms available for plant uptake. Among the nutrients recycled, calcium, magnesium, and potassium are of primary importance in the nutrient return from the forest floor. Much available nitrogen is also obtained from decomposing organics, as well as some phosphorus and sulfur. As plants take up the required nutrients and dispose of wastes, roots and soil exchange ions. The mechanics of such cationic exchange of the forest floor will be discussed in the following review.

The Forest Floor

Organic layers overlying the mineral layers are characteristic features of forest soils. These organic layers, formed from plant and animal residues, are referred to as the litter layers, or forest floor.

Humus substances formed beneath different forest types

show different characteristics which reflect several interacting factors of formation. The kind of vegetation, the species and numbers of decomposing organisms, the macro- and micro-climatic regime, disturbance factors, topography, and makeup of the mineral soil all affect the kind of organic layers formed and their chemical composition.

A classification scheme of forest humus types devised by Hoover and Lunt (1952) could be practical when applied to forest management. The scheme describes three possible layers occurring under forest conditions and designates them as: L, F, and H. The following description (Millar, 1974) relates these different layers to the standardized 01, 02, Al horizon nomenclature:

[L freshly fallen, undecomposed litter.

- (01) F1 dark brown, intact recognizable plant parts, extensively colonized by fungi.
 - F2 greyish, fragmented, compressed recognizable plant parts containing hyphal fragments and animal faeces. Mesophyll collapsed.
- (02) H humus-like amorphous mass of animal faeces, plant and microbial fragments.
- (A1) an intimate mixture of humus and mineral soil.

These layers reflect successive stages of decomposition. The L layer of newly deposited material has not been extensively degraded either physically or chemically. The F layer represents material that has been substantially broken down through biological or physical action. The F

layer material is not yet unrecognizably different in appearance from the originally deposited litter. The loose, amorphous dark material that generally represents the H layer has been considerably altered. Its physical appearance and chemical composition differ markedly from the freshly deposited material representative of the L layer.

The presence or absence of these layers, and the relative incorporation of the H layer into the mineral soil are used to describe the forest floor type. The key devised by Hoover and Lunt (1952) recognized three general types:

(1) Mull: the H layer is absent, and organic materials are intimately mixed with mineral soil; transition between Al and lower horizon is gradual; F layer may or may not be present.

(2) Duff mull: With characteristics of both mulls and mors, this type has H and F layers, with an underlying Al horizon which is similar to that of a true mull; transition from H to Al and mineral soil beneath is gradual.

(3) Mor: There is practically no mixing of organic materials with mineral soil and an abrupt boundary exists between from the surface organic layer and the underlying horizons; the H layer is present except with an imperfect mor.

Litter Production

Large volumes of plant debris, including leaves, twigs,

branches and entire stems, are added annually to forest floors. The rates, times and quantities of addition vary from forest to forest. Bray and Gorham (1964) reviewed world-wide forest litter production and the factors affecting litter production.

The components of litter are described by Bray and Gorham as leaf, fruit, branch, bark, and other. The latter category includes flowers, bud scales, fragments, epiphytes and insects. Leaf material generally constitutes 60-76% of litter, branches 12-15\%, bark < 1-14\% and fruit < 1-17\%. Nonleaf litter components are generally higher for angiosperms than gymnosperms, and warm temperate forests have a higher percentage of non-leaf litter than cool temperate forests. The authors emphasize the difficulty in sampling tree stem litter due to the irregularity of fall patterns, and the great influence of even a single, large tree.

Gymnosperms, Bray and Gorham state, yield about onesixth more total litter annually than angiosperms, although there are some exceptions to this generalization. Besides the variations caused by species type, the authors believe litter fall to be strongly influenced by climate and latitude. For example, litterfall in artic-alpine areas is an order of magnitude less than litterfall of equatorial areas. The higher temperatures, longer growing season and greater amount of insolation during the photosynthetic period in the equatorial areas are of great importance to

litter production.

Litter production is also greatly influenced by site class (Bray and Gorham, 1964). Generally, increased litterfall is associated with better site quality. Hence, site quality estimates can be made from litterfall measurements.

Gloaguen and Touffet (1974) give litterfall values of 3175 kg/ha/year for an atlantic beech (<u>Ilex aquifolium L.</u>) forest in France. The younger stands had a smaller total production than the mature stands. About 86% of the total litterfall was leaf litter.

Egunjobi (1974) measured litterfall in a teak (<u>Tectona</u> <u>grandis</u>) stand in western Nigeria, a dry forest zone. The mean annual litterfall weighed 9024± 882 kg/ha, with about 90% consisting of leaf litter. The volume of teak litter, formed in a warm region (07° 10'N, 03° 52'E), was nearly 3 times the volume of beech litter produced in a cooler region, nearly 35° more northerly.

A jack-pine (<u>Pinus banksiana</u> Lamb) stand in Ontario (46° 21'N, 83° 23'W) in the Great Lakes-St. Lawrence forest region was studied by Foster (1974). Annual litterfall for the 30 year old stand was 3729 kg/ha. Bray and Gorham (1964) indicated 3000 kg/ha/year as average litterfall in cool, temperate conifer forests.

Litter production in the Hubbard Brook Experimental forest in New Hampshire was found to average 5,702 kg/ha/ year according to Gosz et al. (1972). The mixed hardwood overstory contributed 98% of the total production. The shrub layer contributed 68.4 kg/ha/year or 1.2% of the total. The herb layer contributed 45.6 kg/ha/year or 0.8% of the total.

A study by Moir (1972) on lodgepole pine (Pinus contorta Dougl.) stands in Colorado showed litterfall values averaging 4,600 kg/ha/year. About 68% fell as needles, 10% as branches, 18% as cones, and 4% as bark.

Tarrant et al. (1951) studied litterfall in Pacific Northwest forests. Lower values than the averages given by Bray and Gorham (1964) were seen for all species. The highest litterfall was recorded for western red cedar (<u>Thuja</u> <u>plicata</u> Donn), 2145 kg/ha/year, and the lowest for lodgepole pine, 286 kg/ha/year.

Abee and Lavender (1972) studied litterfall in oldgrowth Douglas-fir (<u>Pseudotsuga menziesii</u> (Mirb) Franco) in the H. J. Andrews Experimental Forest in the western Oregon Cascades. The average litterfall was 5,891 kg/ha/year. About 47% fell as needles, 14% as reproductive structures, 33% as wood material, and 6% as hardwoods and mosses.

Litter Decomposition

Leaf and other plant tissues comprising litter may begin to decay while still attached to the living plant. Decomposition in the phylloplane is initially through attack of the easily decomposable sugars exuded from the leaf surface, or released through insect or other structural damage. As the leaf senesces microorganisms can penetrate the cuticle and commence attack on the cell walls (Satchell, 1974). Released materials may then be leached from the canopy through precipitation. Although decomposition processes in the forest canopy have not been widely studied, many of the compounds present in the leaf are utilized by microorganisms and leaf decomposition is probably well started by the time foliage reaches the ground as litterfall (Jensen, 1974). Of course, decomposition of litter at the ground surface is more rapid than decomposition of foliage in the canopy.

Whether in the canopy or at ground surface, certain plant constituents decompose more rapidly than others. Starches, sugars, proteins, and amino acids were considered by Waksman (1938) to be rapidly attacked, and lignins to be resistant to decomposition. The water-soluble substances are utilized readily by the decomposers. Cellulose and lignins are more slowly attacked (Marten and Pohlman, 1942).

Minyard and Driver (1972) studied decomposition of Douglas-fir needles by detecting changes in solubility. They described primary decomposition through changes in solubilities of organic residue components. The authors concluded that the primary processes of decomposition occur on the needle surface with the decomposition of the waxes. Decomposition of the cellular constituents begins as the

waxes are depleted. The thick, waxy cuticle of needles consists of high carbon containing compounds which are ester and alcohol soluble (Millar, 1974). These waxes are slowly weathered while needles are still attached to the tree (Millar, 1974).

Surface litter deposits are subject to severe, nonbiological decomposing action, as well as biological action. Abrasion, wetting and drying, leaching, raindrop and other projectile impact cause fragmentation and chemical alteration. In addition, biological decomposers utilize the organic debris for food as a carbon substrate.

In the forest ecosystem, litter constitutes a large nutrient reservoir. The release of these nutrients for plant use is controlled primarily through the activities of the decomposer biota. The principal decomposers of organic debris are microorganisms, although macroorganisms such as litter-feeding invertebrates also play a large role.

Wide variations in decomposer populations occur under different ecosystems. Seasonal fluctuations of organism populations occur, as well as a successional pattern in a given time over a defined area. Within the litter layers, organic substrates are colonized by successive communities of microorganisms, with each community impact altering the micro-habitat (Gray and Williams, 1971).

Bacteria are found in the largest numbers in leaf

heterotrophs, which must utilize an organic substrate, vary greatly in their physiology and resulting biochemical changes. <u>Bacillus</u> and <u>Pseudomonas</u> are prominent among those using simple carbon compounds, and often have a population flare-up with additions of fresh material to the soil (Gray and Williams, 1971). As the more readily available substances are utilized, these populations dwindle. The next successional wave of bacteria must utilize the more complex substrates remaining. Soluble carbohydrates, starches, pectins and soluble nitrogenous compounds are initially decomposed by bacteria and rapid-growing fungi. Simple polyphenols and other soluble substances also tend to disappear in the primary decomposition stage (Jensen, 1974).

Bacteria initially increase greatly in number after autumn litterfall of deciduous forests. The population increase is correlated with an increase in pH and the disappearance of soluble organics (Jensen, 1974). Saito (1956) determined that the F layer contained the highest bacterial count.

Coniferous litter is initially colonized by bacteria, Ascomycetes, Deuteromycetes, and some Basidiomycetes (Hillar, 1974). Fungal flora play an important role in needle decomposition. The role played by bacteria in decomposition of acid litter is unclear (Millar, 1974).

Actinomycetes are nearly as numerous as bacteria in the organic layers. Organisms such as <u>Streptomyces</u> are able to

attack many resistant substances: cellulose, keratin and chitin (Allison, 1973).

Fungi are also numerous in the soil, and their mass can be greater than the mass of bacteria or actinomycetes. Fungi, such as some Basidiomycetes and Ascomycetes, readily attack cellulose, lignins and other resistant substances (Allison, 1973). Fungal succession follows a pattern similar to bacterial succession. Rapid developers comprise the first fungal successional wave, although bacterial populations are dominant. The second wave of fungal decomposers attack cellulose and similar resistant compounds with fungi now playing the dominant role. Basidiomycetes are the primary organisms involved in the degradation of lignins, and the decomposition usually takes place in the F or H layers, or after the organic material has become incorporated into the mineral soil (Jensen, 1974).

Leaf feeding invertebrates can degrade litter in large amounts, forming substances that stimulate microbial populations (Bocock, 1964). The fragmentation of litter by arthropods increases the surface area. This increased area is subject to enhanced microbial attack as well as greater leaching effects (Gist and Crossley, 1975). Macroorganisms generally graze on freshly fallen materials, but some utilize degraded matter. Many researchers believe that nearly all of the decomposing litter materials will eventually pass through the intestinal tracts of macro- and

mesofauna (Jensen, 1974). The intake of litter organics by arthropods has been related to the content of polyphenols present, and their possible tendency towards formation of less digestible complex protein precipitates (Williams and Gray, 1974).

Lumbricid earthworms are an important group of macro invertebrates. Edwards and Heath (1963, from Lofty, 1974) believed these oligochaetes to be responsible for up to 78% of the total litter disintegration. Earthworms also remove leaf and other litter from the surface and move it down through the litter layer to areas of greater microbial activity (Lofty, 1974).

Cation Exchanging Substances

Ion exchange is an important characteristic of soils since most plant nutrients are obtained through some soilroot exchange mechanism. The interchange between a cation in solution and another cation held by some substance is termed cation exchange capacity (CEC). Several components of soil demonstrate phenomena of adsorption or ion-exchange. Clay minerals often dominate the inorganic fraction with respect to ionic exchange reactions. These clay minerals generally are grouped into 1:1 kaolinitic types, 2:1 expanding smectites, 2:1 non-expanding types and the 2:2 chloritic types. Materials of these groups behave differently in their exchange reactions.

The organic fraction of soils is less precisely defined than is the inorganic fraction. This is due partly to the isolation difficulties of the organic fraction, but also to the extreme multiplicity and diversity of the organic compounds in the soil. The capacity of soil organic materials to bind reversibly exchangeable cations is not well defined (Flaig et al., 1975).

Waksman (1938) stated that humus chemically was composed of certain constituents of the original plant or animal material which was resistant to further decomposition, as well as consisting of compounds resulting from biodecomposition and biosynthesis by the micro- and macroorganisms.

Much later Felbeck (1971) summarized several hypotheses to describe formation of humus materials. The influence of the type of plant materials either strongly affects the kind of humus formed or is incidental to it, depending on which hypothesis is accepted. However, Felbeck emphasizes the fundamental role of microorganisms in all of the theories.

Humus, then, is a mixture of various substances formed through microbial action of various sorts on plant and animal residues. Attempting to characterize the ion exchange phenomena of this heterogeneous organic mass is difficult. Swaby and Ladd (1962) considered humus to be a polymerisate of polyphenols, amino acids, aldehydes, and lignin fractions coupled at random in different quantities and reportions. The relative quantities and proportions of

carboxyl and phenolic groups and resultant CEC will vary greatly from soil to soil.

Adsorption of cations by soil organic materials depends largely on the -COOH and -OH groups present on the internal and external surfaces. The humus material releases H+ ions from these groups and takes on negative charges. This attracts counter ions. The -COOH groups can be dissociated at pH values below 6, while pH values of above 7 generally are required for the dissociation of H+ from -OH groups. For the soil organic fraction, the amount of exchangeable cations depends almost fully upon the pH of the medium (Schuffelen, 1972).

Broadbent and Bradford (1952) suggested that the sites for ion exchange on organic materials arose mainly from carboxyl, phenolic hydroxyls and enolic hydroxyls. Not only is the capacity for ion retention by organic materials a function of the particular structural group, according to Broadbent and coworkers, but also it is a function of the nature of the cation complement present. Metals which exhibit a strong complexing tendency are retained in larger amounts than those which do not have this tendency (Broadbent and Ott, 1957). Humus holds di- and tri-valent metallic cations much more firmly than the monovalent alkali metal cations. Aluminum ions are strongly held by chelation, resulting in a lower apparent exchange capacity (Russell, 1961).

Mechanisms of Ion Exchange

Ions held on exchange sites are held with a different tenacity than those held through chelation. Generally, chelated metals are held strongly by the organic component, although this may not always be true (Allison, 1973). Due to the limited understanding of the chemical make-up of the humus material, it becomes difficult to differentiate between ions held on exchange sites and ions held in some other 'available' manner.

Mortenson (1963) described the holding of metal ions by soil organic materials as 'complexes.' He differentiated these complexes as ion-exchange, surface adsorption, chelation, and complex coagulation and peptization reactions. Natural and synthetic materials have been used to extract metals and organics from soil, and this has been used as evidence of metal chelation. Flocculation, peptization and precipitation reactions have shown that sols and insoluble polymeric complexes and gels are formed through metalorganic materials interaction. Three types of linkages are recognized between functional groups of humic acids and the inorganic soil constituents (Flaig et al. 1975; Alexandrova, 1967):

(1) ionic or heteropolar type with carboxylic and phenolic hydroxyl groups as the participating functional groups leading to formation of humate and fulvate salts. (2) semipolar type forming chelates through coordination linkages with participating amino-, imino-, keto-, and thioether groups.

(3) a type formed by polarization effects and hydrogen bridge linkages with special participation of terminal functional groups forming compounds of the adsorption type.

Amino, imino, keto, hydroxy, thioether, carboxylic and phosphonate groups are present in soil organic materials and are principal chelating donor groups. Polymeric lignins, proteins, tannins, and other polyphenols are present in soil organic matter and contain many ligand groups. These groups probably function mainly in ion exchange, but chelation undoubtedly occurs in molecules containing long chains. Polymeric ligands with large stearic hindrance lack the mobility that small ligands have and consequently do not react with metal ions to the same extent as do small ligands. Similarly, chelation sites on polymers are probably small in number compared with the number of single ligand groups which will bind metal ions (Nortenson, 1963).

Many investigators have studied the relative intensity of retention of one cation over another. Schachtschabel (1940) observed that the strong linkage of the alkaline earth metal ions (Ca²⁺, Sr²⁺, Ba²⁺) was in contrast to alkali metals (Na⁺, K⁺, Mg²⁺) which were held less firmly. The ammonium ion is chemically similar to those of the alkali metals, particularly potassium (Nebergall et al.

1963). Schachtschabel noted that in a solution of equivalent amounts of Ca2+ and NH4+, a selective sorption of those ions on soil humus occurred in a ratio of 92:8. Broadbent (1957) noted that copper was held by complexes which do not combine with calcium. In another study (Thompson and Chesters, 1969), copper was retained to a greater degree than was calcium by both lignin and humic isolates, but was less marked with the humic isolates. This might suggest that weak acidic groups of lignin which originally retained copper but not calcium gained, upon humification, an enhanced acidity which would retain calcium to a greater degree. Further studies on copper and barium by Lewis and Broadbent (1961) showed barium to be held only in the divalent form and by very acidic sites, such as an orthoquinone. Copper was shown to be held as the divalent ion and as the monohydroxide. The authors suggested:

stearic relationships...as the factor causing the adsorption of $CuOH^+$ by some of the phenols, while the most acidic sites are believed to retain $CuOH^+$ in preference to Cu^{2+} , due to the instability of the complexes formed by the latter with two identical ligands of types such as the carboxyl.

Ammonium apparently can be sequestered in soils by a chemical interaction between ammonia and components in soil organic materials. Jannson (1960 from Parsons and Tinsly, 1975) states that under alkaline conditions quinone-amines are formed from auto oxidation/condensation reactions of phenolic constituents with ammonia. Nommik (1965) reviewed ammonia fixation by organic materials and reported that after treatment of organic materials with ammonia, common extractants failed to remove all of the added ammonia; hence, some ammonia has been fixed. Mortland and Walcott (1965) felt that it was probable that the bulk of ammonia sorbed by organic materials is chemically bound. The authors associated degree of fixation with pH. At acid pH values little fixation occurred. Fixation increased gradually as the pH approached neutrality but then increased sharply in alkaline systems. Groups capable of reacting with NH₃ are present in the phenols and quinones derived from organic material decomposition.

Khan (1969) studied the interaction of Mn²⁺, Co²⁺, Ni²⁺, Zn²⁺, Cu²⁺, Al³⁺, Fe³⁺ with humic acids. Titrations of the solutions resulting from mixing metals with humic acids showed complexes being formed. With the exception of Al³⁺ and Fe³⁺, no precipitates were formed with the metals suggesting soluble complexes are formed with the humic acids. Al³⁺ and Fe³⁺ developed precipitates which eventually dissolved as the pH rose above 7. One characteristic of the complex formation was the magnitude of pH drop (from displacement of hydrogen from the functional groups) on the addition of various metals to the humic acids. Equating the tendency of metals to combine with a given ligand with the drop in pH, Khan (1969) found the tendency of the ions studied to form complexes was Fe>Al>Cu>Zn>Ni>Co)Mn. Van Dijk (1971), however, found that there was no major difference in bond strengths at pH 5 for Ba²⁺, Ca²⁺, Mg²⁺, Mn²⁺, Co²⁺, Ni²⁺, Fe²⁺, and Zn²⁺. Pb²⁺, Cu²⁺ and Fe³⁺ were more firmly held, and Al³⁺ appeared to form the hydroxide at pH 5. Flaig et al. (1975) state that generally the intensity of the exchangers follows the lyotropic order. This suggests the dependency of the exchange mechanism on the charge and hydrated size of the ion.

Schnitzer and Skinner (1963a) investigated the complexes formed with Al3+, Fe3+, Ca2+, Mg2+, Cu2+ and Ni2+. Stable, water-soluble complexes were formed with all the metals. As more of the metallic element is complexed, the less water soluble was the substance formed. Further studies (1963b) by the authors showed the important role of carboxyl groups in ion complex formation. Iron uptake was reduced to nearly zero upon methylation of carboxyl groups of a soil organic fraction.

The 1965 paper by Schnitzer and Skinner stated that blocking the acidic carboxyls or phenolic hydroxyls caused significant reduction in Fe3+, Al3+, and Cu2+ retention. Another, more minor reaction occurred between less acidic carboxyl groups and the ions. The authors concluded that alcoholic hydroxyls did not function in any of the reactions studied.

Khana and Stevenson (1962) believed that carboxylic groups bound transition metal ions. Their potentiometric titration results supported the hypothesis that transition

metals form stable complexes with soil organic materials.

Bunzl (1974a) studied the kinetics of ion exchange during continuous, slow addition of divalent lead ions to humic acids and peat. The reaction studied was:

 $\begin{pmatrix} \text{HUMIC} \\ \text{SUBSTANCE} \end{pmatrix} H + \frac{1}{2} Pb^{2+} \rightleftharpoons \begin{pmatrix} \text{HUMIC} \\ \text{SUBSTANCE} \end{pmatrix} - \frac{1}{2} Pb + H^{+}$ At the start of the process lead is at a low concentration. As long as the lead concentration remains fairly low, the rate controlling step is the diffusion of the lead ion through the Nernst film around the ion exchanger particles. The differential equation developed by Bunzl is a function of the ionic concentration, total cation exchange capacity, surface to volume ratio, diffusion coefficients, film thickness, stoichiometric ionization coefficients, and an equivalent separation factor. The rate of uptake is followed as a function of time and yields a characteristic sigmoidal curve. Later experiments (1974b) showed that for the uptake of small amounts of lead the absolute rates decrease if the initial lead content of the sample increases.

Bunzl's equation assumes a proton will be released for each equivalent ion added to the soil organic substances. In contrast, Gamble et al. (1970) considered the degree of ionization of carboxyl groups at the complexing site to be the controlling mechanism of reaction. The authors believed the predominant reaction to be:

$$\begin{bmatrix} HUMIC \\ SUBSTANCE \\ -C-0- + M^{2+} \\ -OH \end{bmatrix} \begin{bmatrix} HUMIC \\ SUBSTANCE \\ -O \end{bmatrix} \begin{bmatrix} 0 \\ -C \\ -C \\ -O \end{bmatrix} + H^{+}$$

where M is some metallic ion. In this equation, each equivalent ion added does not release an equivalent number of protons.

The magnitude of the ion exchange capacity of soil organics is considerably variable. Measurement of this capacity is highly pH dependent. At lower pH values with an excess of hydrogen ions, molecules can easily become protonated and carry a positive charge. Similarly at higher pH values and an excess of hydroxyl ions, hydrogen can be attracted away from a molecule leaving a negative charge. This can easily be diagrammed using a zwitter ion (Noller, 1966):

Pratt (1961) measured the pH dependent cation exchange capacity of surface soils and found that the organic components contribute about 24 times as much pH dependent charge as does clay. Helling et al. (1964) measured CEC of organic materials from Wisconsin soils and found the average CEC to change from 36 to 213 meq/100 gm when increasing the pH from 2.5 to 8.0. Results similar to Helling et al. were demonstrated by McClean and Owen (1969). The latter authors gradually increased the pH of soils by liming and then leaching with potassium chloride, or by using unlimed soils and buffered barium chloride at increasing pH values.

As has been mentioned previously, ligning were shown to have higher absorptive capacities for copper than for calcium. This absorptive capacity is pH dependent, as demonstrated by Thompson and Chesters (1969). The CEC's of ligning were determined using Ca²⁺ and Cu²⁺ as the saturating cation at various pH values. CEC values increased in every case as pH was raised; also, Ca²⁺ as the indicator ion always gave lower CEC values than did Cu²⁺.

The effect of pH on CEC of two forest organic layers (partially decomposed plant materials) was measured by Wells and Davey (1966). The same trend of increased CEC with increased pH was noted. The CEC of a hardwood F layer increased from about 24 meq/100 gm at pH 3 to about 77 meq/100 gm at pH 8. CEC of a pine Fl layer increased from about 5 meq/100 gm to 47 meq/100 gm over the same pH range. Barium was the saturating cation.

Exchange Capacity and Decomposition State

The occurrence of the pH dependent charge of organic materials has created an area of contradiction. Two major theories have arisen concerning relationship of CEC to the stage of humification. An increasing CEC with increasing humification of organic materials extracted from soils is proposed by Kumada (1956), Conversely, the view of

decreasing CEC values of organic materials with increasing humification is held by Sheffer and Ulrich (1960 from Kyuma and Kawaguchi, 1954) who equate increasing polymerization and resulting acidity decreases to increasing humification. Kyuma and Kawaguchi (1964) attempted to clarify this matter. They concluded that at the beginning stages of humification the CEC increases due to carboxylation. However, as humification proceeds the number of hydrophilic acid groups decreases, or CEC decreases.

This recalls the argument of organic matter formation. Isolates termed humic acids, which are base extracted and acid precipitated, contain carboxlic, phenolic, alcoholic, methoxyl, quinoid and carbonyl groups and are weakly dissociated organic acids dominated by aromatic rings (Kononova, 1966). They are large particle weight heteropolycondensates, given particle weights of 30,000 - 50,000 by Flaig (1958 from Kononova, 1966). Dubach and Mehta (1963) reported 'molecular weight' values to 100,000 for humic acids. Fulvic acids, which are base extracted and acid soluble, are believed to consist of weakly expressed rings with a predominance of side chains (Kononova, 1966). Their particle weights are lower than humic acids (Kononova, 1966; Dubach and Mehta, 1963).

Increasing or decreasing CEC with increased humification then is dependent upon the definition of humification. Alexandrova (1966 from Felbeck, 1971) felt humic acids to be

precursors of fulvic acids. If correct, then the higher oxygen content found in the extracted fulvic acids compared to humic acids could be the result of larger carboxlic group content, which would mean greater CEC values with the formation of fulvic acids.

Humic acids are found to have high CEC values of 200 -600 meq/100 gm (Kononova, 1966). Ponomareva (1947 from Kononova, 1966), however, found fulvic acids exchange capacities at very low pH values to be 600 - 650 meq/100 gm, and she concluded that there were more active acid groups in fulvic acids than in humic acids.

Peat soils, which are formed through organic deposition in a bog environment, can have CEC values of 150 or greater. Thorpe (1973) determined CEC of sphagnum moss, reed-sedge and peat humus and found values of 122, 86, and 66 meq/100 gm, respectively. Wilson and Stoker (1935 in Brady, 1974) reported CEC values of 183.8 and 265.1 for a low-lime peat (pH = 4.0) and a high-lime peat (pH = 5.1), respectively.

Litter layers from pine, hardwood and mixed forest stands were analyzed for their cation exchange characteristics by Wells and Davey (1966). The CEC's reported were highly dependent upon the saturating cation, but values ranged from 63 to 154 meq/100 gm for a yellow pine F layer, 36 to 83 meq/100 gm for a 20 year old loblolly pine Fl layer, and 73 to 132 meq/100 gm for the 20 year old loblolly a trend of increasing CEC with depth or degree of decomposition.

Whole forest floor core samples, encompassing all L. F and H layers, were analyzed from the Oregon coast range (Youngberg, 1966). Cation exchange values ranged from 50.1 to 83.7 meg/100 gm. Wooldridge (1968) analyzed L, F and H layers for forests on the east slope of the Cascades in central Washington. Values for the F layer were nearly always greater than for the L layers. Values for the H layers, presumably representing the most humified layers, were always lower than the above-lying layers. Van Cleve and Noonan (1971), however, found different results for interior Alaska forest floors. L, F, and H layers from birch and aspen showed increasing CEC with increasing depth (L through H). One possible explanation might be a greater incorporation of soil mineral materials into the H layers analyzed by Wooldridge. Unfortunately, percent mineral soil or silica values were not reported for either of the studies.

Methods of CEC Determination

Determination of the exchange capacity is conventionally achieved by saturating the soil or exchange-sitecontaining substances with and analyzing for an index cation. The index cation is adsorbed, replacing the original complement of cations. A rinse removes the excess index cation, and the remaining quantity is determined either directly or for CEC must avoid the washing step. Using sodium, calcium or barium as the index ion, the authors developed a procedure that eliminated the washing step. In 1963, the same authors published a paper that reported the magnitude of both salt-retention and hydrolysis errors in CEC measurements. The potential hydrolysis error was found to be usually less than 4% of the CEC. Salt retention errors varied from about 1% to 17% of the apparent CEC and reflect a positive error, compared to the negative hydrolysis error. In their 1964 paper the authors discussed some problems in interpretation of CEC data. They concluded that a balance of the positive error from salt retention and the negative error from hydrolysis of the absorbed cation would be desirable but would be achieved only accidentally.

Frink (1964) studied the effects of wash solvents on CEC determinations. He found that the exchanging substance greatly influenced salt retention and consequently gave high values for CEC. Using a strong acid resin as an exchange medium, CEC values were determined equally well by Na, Ca, or Al saturation, using water, ethylene glycol, methanol, ethanol, n-propinol, acetone, 1-propenal, t-butanol and dioxane as the wash agent. When montmorillonite was the exchanging medium, acetone, t-butanol and dioxane caused considerable salt retention and consequent high CEC values. Frink noted that the low CEC values obtained using the conventional ammonium acetate method might be due to the
solubilization of some of the ammoniated organic matter complex by the lower alcohols.

Smith et al. (1966) used water, methanol, ethanol and isopropanol to remove two saturating salts, ammonium acetate and sodium acetate. Isopropanol was less efficient than methanol or ethanol, and all of the alcohols were less efficient than water. Salt retention was the chief problem.

Wells and Davey (1966) compared CEC values of forest litter layers using different saturating and replacing cations. Highest values were obtained using calcium as the saturating ion. Using Mg, Ba, K, Na, NH_{μ} and H ions as the saturating cation produced lower values, but their relative order was not consistent for all samples. The CEC of Hsaturated samples was nearly the same, regardless of the replacing cation, except in one case with Ba as the replacement ion.

Tucker (1974) studied the displacement of ammonium ion using Li, Na, K, Mg, Ca, Sr and Ba nitrates, alone and as a mixture with KNO_3 . He found the best reagent for displacing adsorbed NH₄+ to be a 2<u>N</u> nitrate solution of K and Ca, with the equivalent ratio of K to Ca in the range of 1 to 3.

Other researchers have developed methods which utilize a direct determination of the saturating ion and, therefore, do not require a replacing ion. Peech et al. (1947) recommended direct distillation of soil samples saturated with mended in the saturation of soil samples saturated with

studied ion exchange reactions in humus using labeled strontium as the index cation. Labeled 89 Sr²⁺ was utilized as SrCl₂. Strontium was determined by liquid scintillation, and Cl by a chloride electrode to yield Sr:Cl ratios and from these the cation exchange capacity was calculated.

In 1950, Black and Smith suggested use of the Lundegardh flame spectrograph for determining exchangeable bases in soils. Soils were treated with ammonium acetate, then from spectra exchangeable bases were quantified.

Carbajal et al. (1973) used x-ray fluorescence to determine CEC using SrCl₂ and BaCl₂ as the saturating ions. A water-wash was utilized. The samples were analyzed for the index ion using an x-ray spectrograph. The authors compared their method to the standard ammonium acetate method, and the method devised by Mehlich (1948). Their results indicated that the x-ray technique produced values intermediate in magnitude to the other two methods, and linearly related.

Choice of the saturating solution index ion may not be as crucial as choice of the reference pH used. The pH dependent charge mentioned previously makes the choice of pH crucial. To adequately reflect the CEC of soils under field conditions, it may be necessary to determine CEC at field pH values. This makes standardization difficult, and comparisons between various research results nearly impossible.

MATERIALS AND METHODS

Study Areas

Litter samples were collected from a wide variety of coniferous and deciduous forests in eastern and western North America. The western samples were collected from the H. J. Andrews Experimental Forest in the Oregon Cascade Mountain range and from several forested areas in the Oregon Coast range. The samples from eastern North America were collected in the fall of 1964 by Dr. C. T. Youngberg while he was on sabbatical leave, and are from the Harvard forest.

All of the 11 Oregon forest sites can be classified into vegetation zones. These zones are primarily based on climax vegetation (Franklin and Dyrness, 1973). Ten of the sites were located in the broad Tsuga heterophylla zone, and one area occurred in the Picea sitchensis zone. The single Picea sitchensis zone stand was located in the coast mountains near Cascade Head, approximately 10 km north of Lincoln City, and less than 1 km inland from the Pacific The elevation is approximately 20 m. The site is in Ocean. an old growth Picea sitchensis (Bong.) Carr. stand located in the Siuslaw National Forest on a steep ocean-facing slope. Extremes in the moisture and temperature regimes are minimal. The climate is uniformly wet and mild with an average annual rainfall of 220 to 250 cm.

The stand composition is mixed Tsure heterophyld; (

Sarg and <u>Picea sitchensis</u>. The understory shrub vegetation is predominantly seedling and sapling sized regeneration from the overstory. The herb layer is mainly <u>Oxalis oregana</u> Nutt. ex T. & G. Some <u>Polystichum munitum</u> (Kaulf.) Presl was present. <u>Rubus spectabilis</u> Pursh was dense on the stand perimeter. This stand will be designated Pisi-Tshe/Oxor for the purposes of this study. The soil is a haplumbrept, with a silt loam formed from fine grained marine sediment (C. Grier, personal communication). The litter layers present and their thicknesses are L(0.5-1.0 cm) and F(0.5-1.5 cm). This forest floor type is a mull. Samples were gathered in early February of 1976.

Three sites were located in the Cascade Head Experimental Forest, about 3 km north of Otis, Oregon and were sampled at the same time as the previous stand. Average annual rainfall is approximately the same as at the <u>Picea</u> <u>sitchensis</u> stand, which is about 10 km distant. The sites are on a gentle, southwest facing slope. Soils are moderately fine textured, acidic deep silt loams derived from highly weathered siltstone and classed as an haplumbrept. In 1935 a mixed <u>Alnus rubra</u> (Bong.)-conifer stand was subjected to three silvicultural treatments. On one plot, all conifers were removed and the remaining <u>A. rubra</u> thinned. On another, <u>A. rubra</u> was removed and the remaining conifers thinned. On the third plot, the mixed 40% <u>A. rubra</u> - 60% conifer stand was untouched. elevations the precipitation falls mainly as snow (Rothacher et al., 1967). Soils vary from shallow and stony with rock outcrops to deep, well developed soils. At the lower elevations soils generally have developed from tuffs and breccias, and those at higher elevations are derived from andesites and basalts (Dyrness et al., 1974).

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The sites represent six forest communities described by Dyrness et al. (1974), and designated as reference stand (RS). The elevations of the sites range from about 450 m at the lowest stand to approximately 950 m at the highest stand.

The lowest site (RS 7) is located at elevations ranging from 450 to 470 m and was sampled in September of 1975. The generally concave slopes have a northwest- (350-360°) aspect and slope gradients varying from 50 to 60 percent. Dark brown gravelly loam overlies a dark brown clay loam. The deep, well drained, alluvial-colluvial eutrochrept soils are derived from breccia, tuff and andesite (Brown and Parsons, 1973). The litter layers present and their thicknesses are the L (1.0-2.0 cm), and F (0.5-1.5 cm) layers. The H layer was generally absent. This forest floor type is described as a mull.

The overstory vegetation is dominated by mixed old growth <u>Pseudotsuga menziesii</u> and <u>Tsuga heterophylla</u> with some <u>Thuja plicata</u> Donn. Seedling and sapling <u>Tsuga</u> <u>heterophylla</u> are abundant in the understory. The minor shrub layer contains such species as Acer circinatum,

The fifth coastal site was located near Tidewater in the Alsea drainage basin about 12 km inland from the Pacific Ocean. The climatic conditions are similar to the other coastal sites. The elevation is approximately 50 m. The stand is situated on a south aspect slope with gradients varying from 30 to 35 percent. The deep, well drained dark brown gravelly loam soil is formed from the Type formation, a thick bedded tuffaceous sandstone with thin intercalations of sandy siltstone (Corliss, 1973). It is classed as an haplumbrept. The litter layers present and their thicknesses are the L (intermittantly present), F (0.5-1.5 cm) and H (0.5-1.5 cm) grading into a highly organic Al horizon. This forest floor type is described as a duff mull.

The overstory is dominated by <u>Alnus rubra</u> intermixed with some <u>Pseudotsuga menziesii</u>. The shrub layer is dense and is dominantly composed of <u>Rubus spectablis</u>. Some <u>Sambucus racemosa melanocarpa</u>, <u>Acer circinatum</u> Pursh and other less numerous shrubs are also present. <u>Polystichum</u> <u>munitum</u> is the dominant species of the herb layer. <u>Oxalis</u> <u>oregana</u>, <u>Maianthemum bifolium</u> and other herbaceous species are present to a lesser degree. This stand will be designated Alru/Rusp/Pomu for this study.

The remaining sites were all located within the H. J. Andrews Experimental forest about 73 km east of Eugene in the Cascade Mountain range. Mean annual precipitation is from 230 cm to 250 cm falling mostly in winter. At higher

According to Franklin and Pechanec (1967), the <u>A</u>. <u>rubra</u> plot has a shrub layer dominated by <u>Rubus spectabilis</u>, with a high frequency of <u>Sambucus racemosa melanocarpa</u> (Gray) McMinn. The herb layer is dominated by <u>Montia sibirica</u> (L.) How. with a high frequency of <u>Maianthemum bifolium</u>. The stand will be designated in this study as Alru/Rusp/Mosi. The litter layers present and their thicknesses are L(0.0-1.0 cm), F(0.5-1.0 cm) and an intermittent H(0.0-1.0 cm.) The Al horizon is high in organic matter. This forest floor type is described as a duff mull.

<u>Rubus spectabilis</u> dominates the limited shrub layer of the mixed <u>Alnus rubra-Pseudotsuga menziesii</u> stand. <u>Montia</u> <u>sibirica</u> is the dominant in the herb layer (Franklin and Pechanec, 1967). This stand is distinguished as Alru-Psme/ Rusp/Mosi. The litter layers present are similar to the preceding stand, and this forest floor type is also a duff mull.

The conifer stand, dominated by <u>Pseudotsuga menziesii</u>, did not have an appreciable shrub layer, and the herb layer was dominated by <u>Maianthemum bifolium</u> with a high frequency of <u>Polystichum munitum</u> (Franklin and Pechanec, 1967). This stand will be designated Psme/Mabi for the purposes of this study. The litter layers present in this stand were similar to the others of this group, but the H layer was generally absent. For this reason, the forest floor type is described

as a mull.

<u>Vaccinium parvifolium Smith and Berberis nervosa</u> Pursh. The herb layer of this moist, very productive site is lush. <u>Oxalis oregana, Polystichum munitum and Linnaea borealis</u> L. are the dominant plants comprising this layer. This stand is part of the <u>Tsuga heterophylla/Polystichum munitum-Oxalis</u> oregana (Tshe/Pomu-Oxor) association.

The next site (RS 2) is located at elevations of 480-500 m and was sampled in September of 1975. The stand is on a generally concave slope with a northwest (285°) aspect, and slope gradients of about 35 percent. Brown to dark brown loam overlies silt loam. The deep, well drained colluvial-alluvial dystrochrept soils are derived from reddish tuffs and breccias (Brown and Parsons, 1973). The litter layers present and their thicknesses are the L (0.5-1.5 cm), F (1.0-3.0 cm) and H (1.5-3.5 cm). This forest floor type is described as a duff mull.

The overstory vegetation consists of old growth <u>Pseudotsuga menziesii</u> and <u>Tsuga heterophylla</u>. The sparse understory consists of tall shrubby layer dominated by <u>Rhododendron macrophyllum</u> G. Don, a low shrubby layer dominated by <u>Berberis nervosa</u>, and a herb layer with <u>Linnaea</u> <u>borealis</u> as the most prevalent species. This stand is part of the <u>Tsuga heterophylla/Rhododendron macrophyllum/Berberis</u> nervosa (Tshe/Rhma/Bene) association.

An eighth site was located at elevations of 600-620 m (RS 10) and was sampled in late January of 1976. The stand

is on convex to concave slopes with a south or southwest aspect (160 to 240°), and slope gradients ranging from 10 to 25 percent. Dark brown, gravelly silt loam with numerous rounded pebbles overlies a brown to dark brown and dark reddish brown clay loam argillic horizon. The very deep, well drained alluvial-colluvial glossoboralf soil developed from reddish breccia and basalt (Brown and Parsons, 1973). The litter layers present and their thicknesses are L (0.5-1.5 cm), F (1.0-3.0 cm) and H (1.0-3.5 cm). This forest floor type is described as a duff mull.

The overstory vegetation is dominated by <u>Tsuga hetero-</u> phylla, with several other conifers and <u>Acer macrophyllum</u> present. The shrub layer is dominated by <u>Rhododendron</u> <u>macrophyllum</u> and <u>Gaultheria shallon</u> Pursh. <u>Acer circinatum</u> and <u>Berberis nervosa</u> are also quite prevalent. The herb layer is scanty with <u>Linnaea borealis</u> being the most prevalent. This stand is part of the <u>Tsuga heterophylla</u>/ <u>Rhododendron macrophyllum/Gaultheria shallon</u> (Tshe/Rhma/ Gash) association.

A dry site was located at elevations of 630 to 700 m (RS 16) and was sampled in September of 1975. The stand is on a slightly convex shoulder/backslope below the ridge crest on the northeast side of watershed 2 (Brown and Parsons, 1973). Steep slopes of 60 to 70 percent have a southwest aspect (190 to 220°). The hapludalf soils are brown to dark brown gravelly silt loam overlying a dark wellowish brown silty clay loam argillic hortzon daveloging in colluvium derived from breccia and andesite (Brown and Parsons, 1973). The litter layers present and their thicknesses are L (1.0-2.0 cm), F (0.5-1.5 cm) and H (1.0-7.5 cm). This forest floor type is a duff mull.

The overstory vegetation is dominated by <u>Tsuga hetero-</u> phylla with some <u>Pseudotsuga menziesii</u> present. A heavy shrub layer consists mainly of <u>Castenopsis chrysophylla</u> (Dougl.) A. DC., <u>Rhododendron macrophyllum</u>, <u>Gaultheria</u> <u>shallon</u>, and <u>Acer circinatum</u>. The herb layer is nearly absent, with the dry site indicator <u>Xerophyllum tenax</u> (Pursh) Nutt. most prevalent. This stand is part of the <u>Tsuga heterophylla/Castenopsis chrysophylla</u> (Tshe/Cach) association.

A site was located at elevations of 880 to 900 m (RS 5) and was sampled in November of 1975. The stand is on an undulating bench with varying aspects (270 to 045°) with a northwest facing slope being the most common. Slope gradients are from 0 to 30 percent. Soils are varied, dystrochrepts and haplumbrepts, but are generally deep, well drained dark brown gravelly loams over silt loams and gravelly silt loams. Pumice and charcoal fragments vary with depth. Parent material is apparently andesitic alluvium-colluvium overlying a layer of previously weathered, and possibly water deposited, silty material (Brown and Parsons, 1973). The litter layers present and their thicknesses are L (0.5-1.5 cm), F (1.0-2.0 cm), and H (1.03.0 cm). This forest floor type is a duff mull.

The overstory vegetation is mainly <u>Tsuga heterophylla</u> and <u>Abies amabilis</u> (Dougl.) Forbes. <u>Rhododendron macro-</u> <u>phyllum, Berberis nervosa, Acer circinatum, and Taxus</u> <u>brevifolia</u> Nutt. dominate the shrub layer. There is little herb layer present. This stand is part of the <u>Tsuga hetero-</u> <u>phylla-Abies amabilis/Rhododendron macrophyllum/Berberis</u> nervosa (Tshe-Abam/Rhma/Bene) association.

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The last H. J. Andrews site was located at 940 to 950 m (RS 3) elevation and was sampled in November of 1975. The stand is located on a slightly concave footslope with a northwest aspect (300°) and slope gradients varying from 15 to 25 percent. The dystrochrept soil is a deep, well drained dark brown gravelly loam over a cobbly silt loam. Parent material is alluvium-colluvium and/or glacial till, derived from andesite (Brown and Parsons, 1973). The litter layers present are L (0.5-1.0 cm), F (0.5-1.5 cm) and H (1.0-3.0 cm). This forest floor type is a duff mull.

The overstory vegetation is mainly <u>Tsuga heterophylla</u> and <u>Pseudotsuga menziesii</u>. <u>Acer circinatum</u>, <u>Rhododendron</u> <u>macrophyllum</u> and <u>Berberis nervosa</u> dominate the shrub layer. <u>Linnaea borealis</u> is the most prominant herb species. This stand is part of the <u>Tsuga heterophylla-Abies amabilis</u>/ Linnaea borealis (Tshe-Abam/Libo) association.

A summary description of the stand characteristics is in Table 1. More complete descriptions of stand

Identification	Reference	General location	Litter layers	Forest floor type
code Alru-Psme/Rusp/Mosi	-	Cascade Head	L F H	duff mull
Alru/Rusp/Mosi	ал — 1	Cascade Head	L F H	duff mull
Alru/Rusp/Pomu	-	Alsea	L F H	duff mull
Pisi-Tshe/Oxor	_	Cascade Head	L F	mull
Psme/Mabi		Cascade Head	L F	mull
Tshe-Abam/Libo	3	H. J. Andrew	IS L F H	duff mull
Tshe-Abam/Rhma/Ben	e 5	H. J. Andrew	ws L F H	duff mull
Tshe/Cach	16	H. J. Andre	ws L F H	duff mull
Tshe/Pomu-Oxor	7	H. J. Andre	ews L F	mull
Tshe/Rhma/Bene	2	H. J. Andre	ews L F H	duff mull
Tshe/Rhma/Gash	10	H. J. Andr	ews I I I	duff mull H

Table 1. Oregon stand characteristics.

vegetation of the ll Oregon sites is presented in Appendix Table 2. A moisture-temperature classification of the sites is given in Table 2. The sites varied from very moist, highly productive stands to dry, less productive stands.

Table 2. Approximate temperature/moisture regime of eleven Oregon forest sites.

Temperature/	Vegetation
moisture group	type
hot/dry	Tshe/Cach
hot/moderately moist	Tshe/Rhma/Gash Tshe/Rhma/Bene
hot/moist	Tshe/Pomu/Oxor
mild/dry	
mild/moderately moist	Tshe-Abam/Rhma/Bene Tshe-Abam/Libo
mild/moist	Alru-Psme/Rusp/Mosi Alru/Rusp/Mosi Alru/Rusp/Pomu Pisi-Tshe/Oxor Psme/Mabi
cold/dry	
cold/moderately moist	End bills film per
cold/moist	
** A	

Samples from watershed 10 of the H. J. Andrews Experimental Forest were gathered by C. Grier and represent a cross-section of several vegetation types. A summary of vegetation types is given in Table 3. Watershed 10 is a 10.24 ha watershed that drains to the west. It contains representatives of communities common to the lower elevation

Substratum unit	Coordinates*	habitat type
1	6-7 7-6	Tshe/Acc1/Pomu
2	12– 10 13– 9	Tshe/Cach
	13-12 13-13 13-14 14-10 14-15	
3	5-2 6-4 11-12 14-17	Tshe/Rhma/Gash
4	4-1	Tshe/Rhma/Bene
5	<u>4</u> -4 4-6 5-б	Tshe/Acci/Pomu
6	3-4	Tshe/Rhma/Bene
7	1-11 2-8 3-13	Tshe/Cach
8	2-10 4-10 4-12 4-13	Tshe/Rhma/Bene
9	7 -8 8-10	Tshe/Rhma/Bene
10	6-12 6-10 6-13 6-14 7-14 8-12 9-13 9-14	Tshe/Rhma/Gash

Table 3. Dominant habitat type of the fifteen watershed 10 substrata.

Table 3. Continued.

Substratum	Coordina	ates* Dominant (50%)	
unit	11-16 11-17	6 7	
11	6-1 ¹ 8-15	4 Tshe/Cach 5	
12	2-6 4-8	Tshe/Rhma/Gash	
13	5-3 6-6	Tshe/Acci/Pomu	
14	9-6 10-6 10-8 10-1(11-9	Tshe/Cacb	
15	6-1 7-2 8-2 8-4	Tshe/Cach	
Code Identif	fication: Acci Bene Cach Gash Pomu	Acer circinatum Berberis nervosa Castenopsis chrysophylla Gaultheria shallon Polystichum munitum	
	Rhma Tshe	a <u>Rhododendron macrophyllum</u> e <u>Tsuga heterophylla</u>	
žu v Coordir	nator ronragant	t exact plot locations on the	

*y-x Coordinates represent exact plot locations on the watershed 10 grid map.

regions of the Tsuga heterophylla zone (Hawk, 1973).

Samples from watershed 10 were gathered after logging was completed, by K. Cromack, Jr. and C. Grier. They represent the dry Tshe/Cach habitat type, stream habitat type and middle Tshe/Rhma types.

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samples from the stream bisecting watershed 10. The standing crop samples represent monthly point samplings of the stream load. The debris was sorted into size categories and bulked into composite seasonal groups. The export samples were gathered by passing the entire stream flow through a net. A wide variation of material is collected in this manner and is sized sorted and classed. Table 4 summarizes the stream sample description.

 Sample type	Sampling period	Sample description	Size class
export	winter	leaves needles	4-16 mm 1-16 mm
		cones	4-10 mm
		twigs fines 75ب fines 250ب all but	4-16 mm 75-250μ 250μ -1 mm
		needles	1 mm
standing crop	summer through spring	bark	4-16 mm
	summer through spring	twigs	16 mm
	summer	needles	16 mm
	summer through spring	wood	4 -16 mma

Table 4. Watershed 10 stream sample descriptions.

The Harvard Forest samples were taken from several

vegetation types. Appendix Table 3 summarizes the stand

vegetation and forest floor type for the eight Harvard forest stands examined. Understory vegetation was sparse in most of the stands, with the exception of two stands with heavy shrub or herb layers. The stands were located on stony loams derived from glacio-fluvial sands and gravels or from granite or granitic gneiss till (Stout, 1952).

Sampling Procedure

A minimum of six litter samples was taken randomly from each Oregon study site. A 10 cm diameter core was cut with a knife through the surface organic layers. The litter was carefully separated in the field and the L, F, and H layers, when present, were identified and separated. The thickness of the layers was also measured. The samples were taken to the laboratory and dried to 63° C. The dried samples were ground to 40 mesh.

Chemical Analysis

Cation exchange capacity was determined using 1 Nammonium acetate at pH 5.5 or 7.0 as the saturating solution. The saturating solution was leached through 1-2.0 gm samples of ground litter contained in filtering gooch crucibles fitted with Whatman #540 filter paper. The leachate was collected and saved for analysis of displaced cations. Excess saturating NH₄+ ions were rinsed from the samples with ethanol. The ammonium-saturated litter was

transferred to 500 ml Kjeldahl flasks and ammonium determined by macro-Kjeldahl distillation as described by Peech (1947). The ammonium acetate leachate was analyzed for displaced bases, Ca, Mg, and K, by atomic absorption spectrophotometry (medel 303, Perkin-Elmer). To prevent interference for Ca and Mg, 1500 ppm Sr solution was used to dilute the aliquot for Ca and Mg analysis. Na or Li 1500 ppm solutions were used to dilute the aliquots for K analysis. The effect of particle size on CEC was measured on samples ground to 20, 40 and 60 mesh.

Total N was determined using the micro-Kjeldahl method described by Jackson (1958). A 0.3 to 0.5 gm sample was digested with a concentrated H_2SO_4 -Salicylic acid mixture, utilizing a CuSO4-Na2SO4-Se catalyst plus sodium thiosulfate. The resulting NH₄+ in the digest was neutralized with NaOH and ammonia distilled into a saturated boric acid solution. The ammonium was titrated with 0.2547 N HCl.

A Corning model 7 pH meter was used to determine pH in a 1:10 litter : water suspension.

Samples from the Quru-Acru-Pist L, Fl and F2 layers were extracted with water at three different temperatures. 100 mls each of hot (84°C), room-temperature (23°C) or cold (2°C) distilled water were used. Samples were extracted for 24 hours with periodic shaking, and maintained at the extraction temperature. Samples were then filtered through #2 Whatman filter paper and the filtrate collected. The samples and filter paper were oven dried at 63° C for 24 hours and reweighed to determine the amount of weight loss. CEC's were determined on the extracted samples. The filtrate collected after extraction was diluted to 250 mls and 50 ml aliquots were titrated with 4.9 x 10^{-3} M NaOH to indicate buffering capacity of the extracted substances.

Entire forest floor core samples from RS 2 (Tshe/Rhma/ Bene) were extracted with six different solvents: Isopropanol, ethanol, acetone, water, 0.003 M NaOH, and 0.25 M HCl. Samples were extracted with 100 mls each of the solutions and shaken for 24 hours. The samples were then filtered, oven-dried and weighed. Cation exchange determinations were made on the extracted litter residues.

RESULTS AND DISCUSSIONS

Decomposition

Cation exchange capacity can represent an index to the cationic nutrient availability. Measurement provides information on the magnitude of cation transfer potential. Exchange capacity of the organic forest floor material is dependent upon the number and nature of exchange sites. As decomposition of the litter proceeds, cation exchange usually increases. As humification becomes more extensive the organic mass becomes increasingly polymerized, and CEC then progressively decreases. Initially, as lignins and other constituents are broken down there is an associated increase in carboxyl groups. But, as extensive polymerization occurs, the number of hydrophilic acid groups is reduced and cation exchange capacity decreases.

The L, F and H layers of the forest floor were examined to determine the effect of decomposition on CEC. Each layer represents a successively more advanced level of decomposition. However, it is unlikely that humification would be sufficiently advanced in any of the layers to have resulted in extensive polymerization and reduction in the number of hydrophilic acid groups. Nearly all sample sites studied showed lower exchange values for freshly fallen material, represented by the L layer, than for the more decomposed F or H layers. An exception was the F layer of the Pist-Tshe/

Oxor site which showed a higher CEC for the L layer than for the thin, intermittantly present F layer. The H layer of the sites sampled generally had higher CEC values than did the overlying L or F layers. Some exceptions to this were found in certain Harvard forest samples where H layers showed characteristically lower CEC values than the overlying F2 layers. A possible explanation is that a greater incorporation of mineral soil occurred in the H layers when the Fl and F2 were split out. This is supported by the percent ash values for those samples, indicating a higher proportion of mineral soil in these H layers.

Summary results for the Alru-Psme/Rusp/Nosi site (Figure 1) showed the difference between the low CEC value for the L layer and the higher CEC value for the H layer to be highly significant (1% level). The F layer had a larger CEC than the L and smaller value than the H but it was not significantly different (statistically) from either layer. Similarly, the difference in the low pH of the L layer and the higher pH values of the F or the H layers was highly significant. The H layer was significantly (5% level) more acid than the F. The base saturation was progressively less with increasing decomposition. The sample variability, however, was too great to show any significant difference between layers.

Results for the Alru/Rusp/Mosi site (Figure 2) showed the difference between the low CEC value for the L layer



Figure 1. Cation exchange capacities (a), pH values (b), and base saturation results (c) for Alru-Psme/ Rusp/Mosi.



Figure 2. Cation exchange capacities (a), pH values (b) base saturation (c) results for Alru/Rusp/Mosi.

and the higher CEC values of the F or the H layers to be highly significant. The H layer CEC was significantly greater (5% level) than the F layer. The pH of the L layer was less acid than the pH of the H layer; the differences were highly significant. The H layer was significantly more acid than the F layer. Sample variability was too great to show any significant difference in pH between the L and the F layers. Base saturation decreased with greater decomposition and there was significant differences between the L and the H layers. Sample variability was too great to show any significant differences between the L and the H layers. Sample variability was too great to show any significant differences between the F and any layer.

The Alru/Rusp/Pomu site (Figure 3) showed a significant increase in CEC in the F layer over the L layer. There were no significant differences between the L or F layers and the H layer which had a high coefficient of variation. The pH and base saturation showed a decreasing trend down through the profile, but there were no significant differences.

The Pisi-Tshe/Oxor site (Figure 4) had only an incipient F layer and no H layer. The CEC of the F layer was less than the CEC of the L layer. The pH decreased from the L to the F layer. The F layer was so thin when present that sampling was difficult. Portions of mineral soil and the L layer were frequently unavoidably collected with the F layer.

-The Psme/Mabi site (Figure 5) was similar to the Pisi-



(a)

(b)

Figure 3.

 Cation exchange capacities (a), pH values (b), and base saturation results (c) for Alru/Rusp/ Pomu.



(a)

Figure 4. Cation exchange capacities (a), pH values (b) for Pisi-Tshe/Oxor.

(b)



Figure 5. Cation exchange capacities (a) and pH values (b), for Psme/Mabi.

pattern of increasing CEC and decreasing pH from the L to the F but no significant differences could be shown.

The Tshe-Abam/Libo site (Figure 6) showed a larger CEC for the H layer than for the L layer; the difference was highly significant. The CEC of the F layer was significantly less than that of the H layer. There were no significant differences between the L and the F layers. The pH on this stand became less acid in the F layer. This trend was seen in many of the other sites located on the H. J. Andrews experimental forest. The L was highly significantly more acid than the F layer, and significantly more acid than the H layer. Although the H layer showed a mean value for pH which was more acid than the F, it was not significantly different. The base saturation trend was one of decreasing bases with increasing decomposition. The base saturation of the L layer was highly significantly greater than that of the H layer. There were no significant differences between other layers.

The Tshe-Abam/Rhma/Bene (Figure 7) site showed increasing CEC values with decomposition. The H layer CEC was highly significantly greater than the CEC of the F or L layers. The L layer CEC was smaller than the F layer, but the difference was not significant. The pH of the F layer was less acid than that of the L layer, but the difference was not significant. The pH of the H layer was lower than the pH of either the L or F layer, and was significantly





Figure 6. Cation exchange capacities (a), pH values (b), and base saturation results (c) for Tshe-Abam/ Libo.



different from the F. The trend of decreasing base saturation with increasing decomposition was repeated at this site. The difference between the low H layer base saturation and the higher base saturation of the L layer was highly significant. There was no significant difference between the F layer and any other layer.

The Tshe/Cach site (Figure 8) CEC increased with increasing decomposition. The difference between the L layer CEC and the CEC of the H layer was highly significant. There was no significant difference between the F layer and any other layer. The pH of the layers increased from the L to the F and decreased from the F to the H. There were no significant differences between the pH of the L layer and any other layer but the difference between the F and the H layers was highly significant. The base saturation data for this site gave no significant differences. The L and F layers had nearly identical mean values for base saturation. The H layer base saturation was somewhat less than either of the above lying layers but the difference was not significant.

The Tshe/Pomu/Oxor site (Figure 9) had no H layer. The CEC values of the existing layers showed increasing CEC with increasing decomposition. The L layer CEC was significantly lower than the CEC of the F layer.

The mean value for the pH's of the L and F layers of this stand showed a slight decrease with increasing decompo



Figure 8. Cation exchange capacities (a), pH values (b), and base saturation results (c) for Tshe/Cach.



Figure 9. Cation exchange capacities (a), pH values (b), and base saturation results (c) for Tshe/Pomu/Oxor.

sition, but the difference was not significant. Base saturation also decreased with increasing decomposition, but the difference was not significant.

The Tshe/Rhma/Bene site (Figure 10) showed increasing CEC values with increasing decomposition, but the differences were not statistically significant. The mean pH values for the L and F layers were nearly identical and the pH of the H layer, although more acid was not significantly different from the other layers. The base saturation of this stand decreased from the L layer to the underlying layers. However, the value for the H layer was slightly higher than for the F layer although the difference was not significant. The L layer base saturation was significantly greater than the F layer value and highly significantly greater than the H layer value.

The Tshe/Rhma/Gash site (Figure 11) showed increasing CEC values with increasing decomposition. The L layer CEC was significantly lower than the CEC of the H layer. The F layer was not significantly different from either the L or the H layers. The mean pH values for this site showed an increase in the F layer. The H layer value was nearly identical with the F layer. The L layer was highly significantly more acid than either the F or H layer pH. The base saturation pattern on this site showed an increase in bases in the F layer commendite the L layer. The mean value for



Figure 10.

Cation exchange capacities (a), pH values (b), and base saturation (c) results for Tshe/ Rhma/Bene.


layers. None of the differences were statistically significant.

The general trend for all sites was increasing CEC with increasing decomposition. Exceptions to this were associated with a lower layer which showed a large incorporation of mineral soil, or with a layer that was so thin that it presented sampling difficulties.

The trend of an increasing number of exchange sites with increasing decomposition during the initial stages of decomposition was suggested by Kyuma and Kawaguchi (1964). The forest floor probably represents initial organic material decomposition. Turn-over times for litter layers of temperate, coniferous forests have been given as from 7 to 10 years. Organic material resides briefly in the L layer, somewhat longer in the F layer and several years in the H layer (Kendrick, 1959). However, this 10 years is only a brief period in the over all residence time of organic material in the soil. Thousands of years have been suggested as the possible residence time for some soil organic materials (Kononova, 1966). Therefore, the surface forest organic material can be considered as representative of initial decomposition stages; stages reflecting advanced polymerization (and resultant fewer exchange sites) would probably not be evident in the surface organic horizons.

The CEC trends shown here are in agreement with those of other workers (Wells and Davey, 1966; Van Cleve and Noonan, 1971).

Statistical analysis on the CEC values generally showed that differences between layers were significant. However, in some cases the sample variability was sufficiently great as to void meaningful statistical inferences. Samples larger than the 10 cm core diameter and/or more numerous samples would help alleviate this problem.

Base saturation and pH values showed even greater variability and statistically significant differences were less evident. The Oregon coast sites showed frends of decreasing pH and base saturation with increasing decomposition, but results from the H. J. Andrews sites were more erratic. Vegetational and environmental differences at the Andrews sites were probably greater.

Nearly all of the Harvard samples showed decreasing pH and base saturation with increasing decomposition. The exception was the Pire stand, which had a higher pH for the Fl layer than for the L layer. There was a good correlation $(r^2= 0.77)$ between pH and base saturation data from the Harvard sites (Figure 12). Results for the Harvard forest are presented in Table 5.

Litter detritus samples from the stream bisecting watershed 10 were gathered and represent standing crop and export debris. Table 6 summarizes CEC values of materials from the standing and by season and by size class. Export sample results in Table 7. The bightst standing



Total 872 80 86.0 30 36.0 30 36.0 30 36.0 30 36.0 30 36.0 30 36.0 30 36.0 30 36.0 30 36.0 30 36.0 30 36.0 30 36.0 30 36.0 30 36.0 30 37.0 30 1.55 5.57 35.07 29.43 4.01 8.38 41.92 41.51 2.83 14.40 28.04 6.32 4.25 ash 23 % Kjeldahl* nitrogen 11.00 2020 2020 37 mmm 3 mmo NIN S 110 10 1.40 740 ч. В. С. 110 0444 PU10-1 -i the Harvard forest samples Lease Leation merro AMED DAT THO DIAN N HOOH 50 23 - 03 1 Mgm CEC 1000 60.837 60.8390 60.8390 60.8390 60.8390 60.8390 60.8390 60.8390 60.8390 60.8390 navor 1 0% 00m0 ren or Crown 50 200 m 101 00 m オオ JJUU S med e fo Chemical characteristics 0.00 3.3 3.671 100000 00000 0000 0000 mH10-3 Hd m н mmtt in -7 Litter layer 1969 H N E E E E JERH しままは NHH H Fr. 口压口 西江 Hu Trom 100 iru-Bela no ur' 白たす Qd. 00 5 R 0 20

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Sample	Size	Season	CEC
description	class	sampled	meg/100 g
Bark	4 mm	summer	88.4
11	11	fall	73.6
II II	11	winter	91.8
"	11	spring	88.3
		x ± s	85.5 ± 8.1
n	16 mm	summer	65.0
I	11	fall	62.5
n	11	winter	67.5
0	П	spring	56.7
		x ± s	62.9 ± 4.6
needles	16 mm	summer	39.5
twigs	16 mm	summer	27.5
n	-U	fall	37.3
n	U	winter	30.9
μ	Hereit	spring	<u>27.4</u>
		x ± s	30.8 ± 4.6
wood	4 mm	summer	45.6
11	11	fall	30.4
*1	"	winter	· · · · · · · · · · · · · · · · · · ·
a statut i	1	spring	44.4
		xts	40.1 ± 8.5
u i i i i i i i i i i i i i i i i i i i	16 mm	summer	51.0
- I	n i Barristan.	fall	45.9
n	11	winter	40.5
11	93	spring	54.3
		x±s	47.9 ± 6.0
	and the second second second second	The second se	and the second

Table 6. Cation exchange capacities of detritus from standing crop samples taken from watershed 10 stream.

crop CEC values are for the bark samples, and the lowest values are for twigs. Sample variability was great and no significant differences could be shown.

	Sample description		CEC meq/100 g	
	all but needles		68.4	
	cones		62.2	
	bark		57.8	
	leaves		52.5	
	fines 75		50.9	
	needles		45.2	
	twigs		41.7	
100 - 10 - 10 - 10 - 10 - 10 - 10 - 10	A CONTRACTOR OF	States of the Wood of the State of the States of the State	These hards to be an and the second of the second	

29.0

Fable 7.	Sample description	s and corresponding cation	
	exchange capacitie	s of stream export samples.	

fines 250

Export samples showed highest CEC values for a composite sample containing everything but needles. Very small fines (<250,) had the lowest CEC, probably because of the high percentage of ash (B. Buckley, personal communication).

Samples which had zero-time stream residence had very low CEC values (Table 8). Of these, bark showed the highest value and wood and chips showed the lowest value.

The effect of removal of water soluble substances on litter cation exchange capacity was determined on Harvard must litter. The samples were from the Quru-Acru-Pist is a subscription of the Quru-Acru-Pist extreme to the samples water of three different is a subscription of three different

Table 8.	Cation exchange	capacities of	zero-time	watershed
	10 stream decomp	osition study.	•	

Sample description		CEC meg/100 g	
wood		4.8	
chips		4.9	
twigs		21.5	
bark		44.4	

extraction temperature is given in Table 9. Weight loss graphed against extracting temperatures is presented in Figure 13. The extracting solution was titrated to determine the extent of buffering. The results are given in Figures 14, 15, and 16.

The data indicate that weight loss is directly related to the temperature of the extracting solution. The relationship is nearly linear for the L layer. There is a distinct break at 23°C for the Fl and F2 layers. The stage of decomposition did not appear to affect the rate of weight loss, although the magnitude differed significantly between layers. At 84°C, extraction, the weight loss of the L layer was highly significantly greater than that of the F2 and significantly greater than the F1. At 23°C extraction the weight loss of the L layer was highly significantly greater than the weight loss of the F1 or F2. There was no significant difference between the weight loss of the F1 or F2 layers at 23°C. At 2°C extraction, the weight loss of the

Table 9. Cation exchange capacities of forest litter after being extracted with distilled water at 3 different temperatures.

Sample description	Extraction temperature	Percent weight loss	CEC meg/100 g
2-L	84 C	24.0	38.0a*
n	23 C	13.0	48.4b
	2 C	10.1	46.9b
	untreated		50. 0b
2-Fl	84 C	19.5	47.5a
0	23 C	7.7	54.8b
11	- 2 C	- 6.5	53.7b
11	untreated	2000 - 100 -	54.7b
2-F2	-0 - -C	10-9	71. 9a
-H	23-0	8.6	76.5b
11	2 C	7.1	75. 8b
"	untreated		74.1b

* values followed by the same letter are not significantly different at the 5% level.

L layer was highly significantly greater than that of the Fl layer, and significantly greater than that of the F2 layer. There was no significant difference between weight losses of the Fl or F2 layers.

The CEC of the extracted samples (Table 9) showed some unusual differences. The L layer extracted at 84°C had a highly significantly lower CEC than the CEC of the same sample extracted as 3° or 2°C. The room temperature and









cold temperature treatment did not significantly alter the There were no significant differences between either CEC. of the two samples extracted at the lower temperature or of the CEC determined on non-extracted samples. The pattern was similar with the Fl and F2 layers. The pH of the extracted solutions tended to become more acidic as temperature of the extracting solution was increased. Upon titration the 84°C extractant solutions generally yielded sigmoidal curves, which indicated monobasic substances (Wright and Schnitzer, 1963) with a higher buffering capacity than the solutions extracted at lower temperatures.

suspension fibrations to level off around pH 8. The litter samples which were subjected to the 84°C water extraction all showed signs of chemical alteration. The litter became darker, forming a blackish suspension of finer sized particles which settled into a densely compacted mass upon filtration. The samples extracted at 20 and 230 retained their color and over all appearance. Although the cation exchange capacities of all the samples extracted at 23°C

were slightly increased over those extracted at 2°C, as

mentioned before the ulfference was not significant. The

itentificantly loved than College of samples extracted at

for securities and cold tagger ture. This could indicate

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that the chemical alteration which was apparent in the 84°C extracted samples might involve a polymerization which decreased the number of exchange sites.

From the data it is seen that water soluble substances of forest litter contribute between 7 and 24 percent of the total weight of the litter. The substances extracted with 23°C or 2°C water have a limited buffering capacity. The substances extracted at 84°C have a strong buffering capacity and are highly acidic.

Residue of litter samples extracted with various liquids had significantly different CEC values and showed differences in weight losses. The sample material was an entire core, I. e., a composite including L. F and H layers. Weight loss and CEC data are given in Table 10. Samples treated with organic solvents generally lost less weight than samples treated with acid or base. The order of weight loss and resultant CEC was HCl>NaOH}ethanol>H₂O}isopropanol> acetone. There was no significant difference between amount of weight loss and resulting CEC values of the HCl or NaOH treatments. Ethanol and water treatments did not give significantly different weight losses or CEC values, nor did ethanol, acetone or isopropanol treatments.

Vegetational Differences

Felbeck (1971) summarized several theories about organic matter formation. One theory proposes that the

Extracting solution	Percent weight loss	CEC meg/100 g	-
untreated		50.6	
.25 N HC1	9.9	39.8	
.003 N NaOH	8.9	35.3	
ethanol	7.4	33.8	
water	8.1	32.0	197 - TC 6
isopropanol	6,5	28.7	
acetone	7.0	28.3 -	100100100
the second se	A MIN SHITTAKE A MINING AND A MINING AND A MINING AMINING A MINING		1.4

Table 10.	Cation exc	change	car	acities	of	residue	from	litter
	extracted	with	six	differen	nt :	solutions		

parent vegetation has little effect on the kind of organic

matthem or not this is true in

the long term ion attion of organic materials, it is nearly certain to be false in the initial stages. In the beginning stages of forest floor decomposition the residual parent plant material would be expected to exert a strong influence on the kinds of organic substances present. Characterization of the number of exchange sites, or CEC of the material, might indicate one aspect of the nature of the substances formed.

Because the H layer was non-existent at several sites, the sums of L and F layer CEC's were used to rank the eleven Graden sites (Table 11). This ranking showed a relationship between the cumulative CEC and the timber site quality of the stand. From the most productive and was under

	Vegetation type	17 C text	L & F meg/10	CEC D0 g	
	Tshe/Pomu/Oxor	7	140.6	a*	
	Pisi-Tshe/Oxor		133.9	ab	
	Psme/Mabi		126.8	ab	
	Alru/Rusp/Mosi		115.7	bc	
	Alru-Psme/Rusp/Mos1		114.6	be	
	Alru/Rusp/Pomu		- X141.2.	be	
	Tshe/Rhma/Bene		113.6	be	
	Tshe/Rhma/Gash		107.8	C	
	Tshe-Abam/Libo	-Gen	104.4	cd	
	Taha/Gachan a		98.6	Ted	
	Tshe-Abam/Rhma/Bene		95.6	d	
in the	the second se	a service of the serv	a second a second second	and the set of the set of the	100 ANT 200

Table 11. Ranked cation exchange capacity values for eleven Oregon forest sites by sums of L and F layers.

*values followed by the same letter are not significantly different at the 5% level.

Tshe/Pomu/Oxor vegetation. This stand has a lush herb layer. The vegetation type occurring on this stand usually is found on site classes I or II (Dyrness et al. 1974). Tshe/Pomu/Oxor had the highest cumulative CEC, highest L layer CEC and highest F layer CEC.

Cumulative CEC values for the Tshe/Pomu/Oxor, Pisi-Tshe/Oxor and Psme/Mabi stands were not significantly different. These three stands represent good sites. probably the best timber sites of all of the sites in locations.

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Values for the L layer alone (Table 12) show the Tshe/ Pomu/Oxor stand with highest CEC, although it is not significantly different from Pisi-Tshe/Oxor or Psme/Mabi. The F layer CEC value for Tshe/Pomu/Oxor (Table 13) was significantly higher than any of the other vegetation types.

Table 12. Ranked cation exchange capacity values for eleven Oregon forest sites, L layer.

Vegetation type	CEC meg/100 g
Tshe/Pomu/Oxor	66.3 a*
Pisi-Tshe/0xor	66.2 a
Psme/Hab1	58.8 ab
Ton	
Aligu-Folie/ Luspitioni	Barry P
Tshe/Rhma/Gash	51.9 b
Tshe-Abam/Libo	50.7 в
Alru/Rusp/Mosi	50.7 bc
Alru/Rusp/Pomu	50.1 bc
Tshe/Cach	46.8 bc
Tshe-Abam/Rhma/Bene	44.9 c
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* values followed by the same letter are not significantly different at the 5% level.

The poorer sites, best represented by the Tshe-Abam/ Huma/Bene ind the cash Estimations, always ranked lowest in cumulative of a lower CEC or F layer CEC. Tshe-Abam/

Vegetation type	CEC meq/100 g
Tshe/Pomu/Oxor	74.8 a*
Psme/Mabi	68.0 ъ
Alru/Rusp/Mosi	64.1 b
Alru-Psme/Rusp/Mosi	62,2 bc
Alru/Rusp/Pomu	62.1 c
Tshe/Rhma/Bene	60.5 c
Pisi-Tshe/Oxor	58.6 cd
Tshe/Rhma/Gash	56.2 . cd
She-Abam/Libo	54.6 cd
Tshe/Cach	53.7cd
Tshe-Abam/Rhma/Bene	50.0 d
	The second se

Table 13. Ranked cation exchange capacity values for eleven Oregon forest sites, F layer.

* values followed by the same letter are not significantly different at the 5% level.

northerly aspects at about 890 m elevations. This association has the most sparse herb layer of any community, and <u>Xerophyllum tenax</u> is typically present. The site class range for this association is III - IV (Dyrness et al. 1974). The stand sampled was probably on the lower quality side of this class range. The Tshe/Cach association is usually found on brushy, xeric sites which are either exposed or just off ridge tops. <u>Xerophyllum tenax</u> and <u>Pinus</u> <u>lambertiana</u> are present with this association, which is found on site classes III - IV. RS 16 is probably a less severe example of this association. Both of these vegetation types had L + F CEC values almost one third less than those of the Tshe/Pomu/Oxor site.

Samples gathered from watershed 10, and representing 15 substrata units are ranked in Table 14 in order of decreasing CEC values. These are mixed organic layer camples and represent a composite of L + F + H layers when the layers were present. The highest mean CEC was seen substratum 1, which is dominated by the <u>Tsuga hetero-</u> phylic iter direinatum/Polystichum munitum association. The association ted distribution and is found on site Howave, substratum 5 is also

bottom of the ranked list. This suggests that CEC of entire (composite L + F + H) cores are not sufficiently discriminating to be used as indices to quality of site. A thick layer that had a lower CEC would easily mask a thin layer with a higher CEC. Also, variations between samples were very high, and only the extreme top and bottom substrata were significantly different statistically from each other.

strend atton, yet 5 is found near the

Entire composite L + F + H core samples from watershed 10 (Table 15) were gathered after logging. These represent

The fact of the state and the first des fur types and also

rere highly variable. No similicant diffrences between

the three but base uped

Substrata	CEC
unit	meg/100 g
number	XIS
1	62.9 ± 7.4 a*
8	59.0 ± 4.8 a
. 11	52.8 ± 11.7 ab
10	52.5 ± 13.5 ab
3	52.5 ± 7.8 ab
12	52.1 ± 8.0 ab
1	51.1 ± 9.4 abc
13	50.0 ± 19.7 abc
-14	49.9 ± 4.5 bc
2	49.8 ± 7.4 bc
9	48.9 ± 8.5 bc
4	47.9 ± bc
6	46.4 ± 11.5 bc
5	45.9 ± 3.8 bc
15	43.7 ± 8.3 c

Table 14. Cation exchange capacities of fifteen watershed 10 substrata units.

* values followed by the same letter are not significantly different at the 5% level. (See Table 3 for identification of dominant habitat types of 15 substrata.)

Table 15.	Cation	exchange	capacities	of	watershed	10	post-
	loggin	s samples					

Sample description	CEC meq/100 g
dry site Cach type	40.1 ± 2.4a*
stream site habitat type	49.2 ± 10.3a
Rhma type middle area	42.3 ± 8.8a

mean 1 standard deviation; values followed by the same letter are not significantly different at the 5% level.

Rethodology

an ethanol rinse in the CEC determinations reported here. No significant differences could be seen between direct distillation of the samples or distillation of a displacing HCl solution (Table 16).

Table 16. Cation exchange capacities of bark with and without using HCl as the displacing solution.

Method used	CEC mea/100 g
Direct distillation	30.4
HCl displacement	29.1

From data given earlier (Table 10) it can be inferred

that the difference in CEC over use of water. Both

solvents extract out 7 to 8 percent by weight of the litter material.

Variations in results from replicate samples were great, especially for determinations of base saturation or pH. Larger sample size and more replicates might reveal differences between the litter layers or vegetational types which would be statistically significant.

SUMMARY

(1) Forest floor litter from eleven Oregon sites showed increased cation exchange capacity (CEC) with increased decomposition. CEC's of litter from eastern U. S. forests showed similar trends except where lower CEC values were associated with high ash contents of an Univer.

(2) Base saturation of the different litters was highly variable but generally decreased with decomposition.

(3) Type of vegetation influenced the magnitude of the CEC of the different litter layers. Litter layers from better sites had greater CEC values than litter layers from moorer timber sites.

(4) Less material (by weight) was extracted from litter by organic solvents than by H₂O, NaOH or HCL. The water and organic extracted residues had lower cation exchange capacities than either the HCL or NaOH extracted residues.

(5) Hot water extracted more material (by weight) than room-temperature water or cold water. Extracts from hot water treatment were more highly buffered and more acidic than extracts from cooler-temperature water treatments.

(6) Detritus materials sampled from a small stream were highly variable as to CEC--bark residues gave highest CEC values and twigs gave lowest.

(7) Litter freshly fallen into the stream had lover

CEC values than similar residues with longer residence times in the stream.

(8) Entire L + F + H core samples were insufficient for determining the differences vegetation types may cause in CEC values of forest floor litters.

(9) Direct distillation of ammonium saturated litter different CEC values from use of H⁺ as the designing ion.

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ppendix Table 1.	Scientific	and comm	ion names	of plants
	involved in	1 this st	udy.	

Appendix Table 1. Scientific and com involved in this s	mon names of plants tudy.
Scientific name	Common name
Abies amabilis	Pacific silver fir
Acer circinatum	vine maple
Acer macrophyllum	bigleaf maple
Acer rubrum L.	red maple
Acer saccharun Marsh.	sugar maple
Achlys triphylla (Smith) DC	deerfoot vanillalea
Alnus rubra Bong.	red alder
Aralia nudicaulis	
Berberis nervosa Pursh	Oregongrape
Betula lutea L.	yellow birch
Carex Leptopoda	nerrowleaf or the
Castenopsis chrysophylla (Dougl.) A.DC.	go lden chinkapen
Chimaphila umbellata (L.) Bart.	western prince's pi
Coptis laciniata Gray	cutleaf golden thre
Cornus candensis L.	bunchberry dogwood
Cornus nuttalli Aud. ex T. & G.	Pacific dogwood
Disporum smithii (Hook.) Piper	Smith's fairybells
Euryhnchium oreganum (Sull.) J. & S.	
Euryhnchium stokesii	
Galium triflorum Michx.	sweetscented bedstr
Galutheria shallon Pursh	salal
Holodiscus discolor (Pursh) Maxim.	creambush oceanspra
Isothecum spiculiferum	

Appendix Table 1. Continued.

Scientific name	Common name
Linnaea borealis L.	twinflower
Luzula parviflora	woodrush
Lycopodium complanatum	
Maianthemum bifolium	
Mitchella repens	
Mnium insigne	
Montia sibirica (L.) How.	western springbeauty
Oxalis oregana Nutt. ex T. & G.	Oregon oxalis
Picea abies	
Picea sitchensis	Sitka spruce
Pinus lambertiana Dougl.	sugar pine
Pinus resinosa	red pine
Pinus strobus L.	eastern white pine
Plagiothecum denticulatum	
Polysticum munitum (Kaulf.) Presl.	swordfern
Pseudotsuga menziesii (Mirb.) Franco	Douglas-fir
Pteridium acouilinium (L.) Kuhn	bracken fern
Quercus rubra L.	northern red oak
Rhododendron macrophyllum G. Don	Pacific rhododendron
Rhytidiadelphus loreus (Hedw.) Wasnst.	
Rubus parviflorus Nutt.	thimbleberry
Rubus spectabilis Pursh	salmonberry
Sambucus melanocarpa	elderberry

Appendix Table 1. Continued.

Scientific name

Smilacena racemosa

Symphoricarpus mollis Nutt.

<u>Taxus brevifolia</u> Nutt. Thuja plicata

Tiarella unifoliata Hook.

talis americana

121 Little ovatum Pursh

Tsuga canadensis (L.) Carr. Tsuga heterophylla (Raf.) Sang

Vancour ria nezandra (Nook.) Morr. 2 Dec.

Hard I and Annother

<u>Viola Sempervirons</u> Greene <u>Xerophyllum tenax</u> (Pursh) Nutt. creeping snowberry western yew western red cedar western coolwort

Common

name

white trillium eastern hemlock

western hemlock

red huckleberry

white inside-outflower

evergreen violet common beargrass

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	He/Ru	oW/dst	JSP/PG	she/ox	ab1.	Dam/L1	oath/R	Lon 2	CO/nuc	a/amc	nav Ge
	d-nath	AT TUKR	IIru/R	F-1sta	Psme/lit	Ishe-Al	rshe-Al	Tshe/Cu	Tshe/Po	Tshe/R	Tshe/R
				and a second	and and				(a)(*)		
Abies anabilis		X	in. X			X:	x	x	x	x	x
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Berberis nervosa			-	1. 4. 8	1	x	X	X	x	X	x
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Coptis laciniata	17 mg • * 2 mm			1. 28	-	X			1	X	1. 1
Cornus nuttalli			- 22					x		-	x
Disporum smithii		X									
Eurhynchium creanna	X	X			X						
Eurhynchium stokesii	- control	X				2	ALT.			-	
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Linnaea boreaits	Same I	121 -	5-1-			X	X	X	X	X	X
Luzula parvillora					X						
Malantherum bifollum	x	X	X		X	-					_
Mnium insigne		<u>x</u>									
Montia sibirica	X	X	×.								
Oxalis ore-tanum		~	X	X					X		
Picea sitemensis	X	<u>, x</u>			X						*
Pinus Tambercrana											~ ^
Plagiothedun centiculatum											
Polystichum nunitum	X	<u> </u>	X	×	X	X			X		X.
Pseudotsufa hendlesii	X		X		7.	X	X	_X_	<u>X</u>		X
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Tarus brevifolia							Y	Y		Ŷ	r
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Trillium ovatum					x						
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Viola sempervirons											

Appendix Table 2. Principle vegetation present on the eleven Oregon forest atands.

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