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<u>Gody Spycher</u> for the <u>Master of Science</u>
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Title: <u>EXTRACTABLE FORMS OF Al AND Fe IN ACID WESTERN</u>

<u>OREGON SOILS</u>

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E. G. Knox

Extractable forms of Al and Fe were studied in five soils from

the Coast Range, and in two soils from the Willamette Valley in

Oregon.

Exchangeable Al was determined in a way which permitted a

comparison of three different methods for its determination. Values

for exchangeable Al obtained by the method of limited leaching by Lin

and Coleman (1960) agreed closely with those obtained by the method

of Skeen and Sumner (1965) which consists of successive extractions

and extrapolation to obtain the exchangeable Al content. Values for

exchangeable Al measured by the method of exhaustive leaching pro-

posed by Dewan and Rich (1970) exceeded the Coleman values in differ-

ent amounts depending on the amount of exchangeable Al present, and

on the final slope of the extraction curves. Steep slopes were found in

coastal soils containing amorphous aluminosilicates, indicating that

these soils have a strong supplying power for exchangeable Al. From the shape of the Al extraction curves it was concluded that two different forms of Al were extracted by the method of successive extractions, namely, a readily exchangeable form, and a form that is slowly released and which presumably results from mineral solution of amorphous oxides or from Al-organic complexes.

In soils with a high base saturation good agreement between both the Coleman and the Rich values for exchangeable cations with the neutral salt CEC was observed. In soils in which Al is the dominant cation of the exchange complex, the neutral salt CEC was from 2 to 3 meq lower than the Coleman value for exchangeable cations. These differences were attributed to errors in the CEC determination due to hydrolysis. The Rich values for exchangeable cations exceeded the neutral salt CEC by amounts as high as 10 meq/100g. It was therefore concluded that Rich's method to determine exchangeable Al furnishes values that are not compatible with other standard methods.

The ratios of humic to fulvic acid extracted by pyrophosphate were higher in grassland soils than in forest soils. The total amounts of Al and Fe correlate fairly well with the organic carbon extracted by pyrophosphate. The contents of Al and Fe were much higher in fulvic acid than in humic acid, but this was ascribed to the formation of soluble complexes of previously organically bound Al and Fe with pyrophosphate appearing in the fulvic fraction. It was concluded that

pyrophosphate extractable Al and Fe represent a rough estimate of the amounts of Al and Fe involved in cation bridges.

The ratio of Al or Fe to organic carbon extracted by pyrophosphate increased with depth. This could be due either to a change in organic matter composition, or a result of increased dissolution of inorganic amorphous oxides in lower horizons.

In the top horizons of soils high in organic matter the absolute amounts of pyrophosphate extractable Al and Fe were much higher than in soils low in organic matter. However, the metal to organic carbon ratios in the top horizons were fairly similar. This suggests that the proportions of organic matter bonded to inorganic surfaces by cation bridges have similar contents of polyvalent cations. It was therefore concluded that differences in organic matter accumulations should be explained in terms of the kinds and amounts of inorganic surfaces available for organic matter adsorption in a soil. In previous work, the coastal soils with high organic matter accumulations have been shown to contain amorphous alumino-silicates. These minerals are unique in that they combine negative charges and an aluminous surface with a high specific surface area. Thus, they favor the formation of all the known types of organo-mineral bonds, except anion exchange.

The oxalate and dithionite extractions did not yield much information, and were difficult to interpret due to uncertainties regarding

their presumed specificity for pedogenetic oxides. However, dithionite in conjunction with pyrophosphate appears to be useful for the chemical identification of spodic horizons.

The classification of the Knappa and the Nehalem profiles did not correspond to the official series classification. The Knappa profile was classified as a Typic Dystrandept instead of a Pachic Haplumbrept. The Nehalem profile was found to be a member of the Fluventic Hapludoll instead of the Fluventic Haplumbrept subgroup.

Extractable Forms of Al and Fe in Acid Western Oregon Soils

by

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Professor of Soils
in charge of major

Redacted for privacy

Head of the Department of Soil Science

Redacted for privacy

Dean of Graduate School

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Typed by Cheryl E. Curb for   Gody Spycher

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INTRODUCTION

Considerable research has been accomplished on the chemistry, mineralogy, and fertility of the soils in the Coast Range of Oregon. These studies included the thin section micromorphology (Norgren, 1962), the state of weathering (Rojanasoonthon, 1963), mineralogy, chemistry, and fertility relationships (Jenne, 1961), and chemical and mineralogical relationships of coastal Andosols (Franklin, 1970). Meurisse (1972) determined site qualities for timber production, and studied chemical characteristics of some coastal soils.

Areas of interest which have been somewhat neglected in the past include, among others, the exchange acidity, the large organic matter accumulations and, to a lesser extent, the distribution of pedogenetic oxides of these soils.

The specific objectives of this study were:

1. To characterize the soil acidity of some coastal soils.

2. To compare different methods to determine the exchange acidity.

3. To study the relationship of organic matter accumulations with Al and Fe.

4. To determine the distribution of the pedogenetic oxides of these soils.

5.   To relate the Fe, Al, and organic matter distributions to the genesis and classification of these soils.

LITERATURE REVIEW

Exchange Acidity

The concepts of the nature of soil acidity have undergone considerable changes during the past decades (Jenny, 1961a). The importance of exchangeable Al in soil acidity, after first having been demonstrated by Veitch (1902) and later by Paver and Marshall (1934), became established only in the early 1950's. At that time the work of Chernov in Russia became known (Jenny, 1961a), and other workers began to study acidified clays (Harward and Coleman, 1954; Low, 1955). In this early work it was shown that H-saturated clays are unstable systems which change spontaneously to a condition of predominant Al-saturation due to the interaction of protons with the clay lattice. This results in a breakdown of the lattice edges and in a release of lattice ions into an exchangeable state (Low, 1955; Coleman and Craig, 1961). The liberated Al upon further aging, hydrolyzes, polymerizes, and accumulates as hydroxy Al in the interlayer space of layer silicates (Jackson, 1960). The formation of interlayers and coatings in acidified clays and in sesquioxide-clay mixtures has been confirmed in numerous studies (Rich, 1960; Coleman and Thomas, 1964; Coleman et al., 1964). These interlayer materials carry positive charges under acid conditions (Jackson, 1963); hence, they block exchange sites resulting from the negative charge of the lattice

clays. . This leads to a reduced neutral salt cation exchange capacity,

whereas the buffering capacity in the pH range from 5 to 8 is increased.

Based on the acid strength of the proton-retaining site, Jackson

(1963) proposed five buffer ranges for soils corresponding to (I) ex-

changeable protons, (II) exchangeable Al (aluminohexahydronium),

(III) strong hydroxy Al polymers and humus carboxyl, (IV) weaker

hydroxy Al polymers and humus phenolic groups, and (V) humus

alcoholic groups, silicic acid-OH, and gibbisitic-OH. It was shown

that the first three ranges can be distinguished by potentiometric titra-

tions in acidified clays and soils (Schwertmann and Jackson, 1963;

Volk and Jackson, 1964). In natural systems, appreciable amounts of

exchangeable hydrogen have been found only in cat clays (Sulfaquepts)

containing free sulfuric acid, but not in other soils (Lin and Coleman,

1961; Volk and Jackson, 1964; Dewan and Rich, 1970). It is generally

agreed that the exchange acidity of soils consists almost entirely of Al.

It should be mentioned that the definition by Coleman and Thomas

(1967) of the term "exchange acidity", namely, the portion of soil

acidity replaceable by neutral, unbuffered salts, is used in this study.

Exchange acidity includes thus, both exchangeable Al and exchangeable

H extracted by a neutral salt.

Exchangeable Fe seems to play but a minor role in exchange

acidity. Dewan and Rich (1970) reported less than 0.2 meq of exchange-

able Fe per 100 grams extracted from their soils with KCl.

Schwertmann (1970) measured up to 2.5 meq exchangeable Fe/100

grams in Podzols, but most of this Fe was present in the form of

soluble organic complexes.

The acidic properties of soils are influenced to some extent by

their mineralogical characteristics. Page et al. (1965) suggested

that difficultly replaceable Al-polymers form more readily in the inter-

layer spaces of vermiculitic soils than in montmorillonitic soils. In

Al-bentonite and similar clays, neutral salts displace amounts of Al

closely equivalent to their cation exchange capacity (Lin and Coleman,

1961). However, in vermiculite-like clays, KCl has been found to dis-

place only 3/4 or less of the adsorbed Al, but released acidity in con-

siderable excess of the Al exchanged (Rich, 1960; Hsu and Bates, 1964).

Similar results were reported by Kaddah and Coleman (1967) who con-

cluded that hydrolysis of Al occurs in the interlayer spaces of vermi-

culite. The protons released by this internal hydrolysis are exchanged

against the cation of the neutral salt (Dewan and Rich, 1970). Thus, at

a given content of hydroxy Al and Fe the amount of exchange acidity is

least reduced in montmorillonite, intermediate in vermiculite, and

highest in kaolinite (Coleman and Thomas, 1967); or expressed in

terms of the ratio of exchange acidity/total acidity (at pH 8.2), it is

highest for montmorillonite, intermediate for vermiculite, and lowest

for kaolinite. Coleman et al. (1964) working with bentonite found that

hydroxy Al reduces the exchange acidity more effectively than

hydroxy Fe.

Data concerning exchangeable Al in soils that contain allophane as a major mineral are very limited. Birrel (1962) examined the surface acidity of subsoils derived from volcanic ash deposits. He concluded that allophane present in earlier weathering stages develops marked surface acidity, and that a moderate degree of weathering produces allophane showing the highest acidity. Intensive weathering, resulting in the predominance of kaolin minerals, significantly reduced the acidity. Igue and Fuentes (1972) measured exchangeable Al in volcanic ash soils of Costa Rica. These authors found exchangeable Al as determined by successive extractions with unbuffered salt solutions to be relatively low, and indicated that exchangeable Al seemed to increase with weathering intensity.

The contribution of organic matter to the exchange acidity of soils is presumably insignificant. The functional groups of organic matter, with the exception of carboxyl and phenolic groups, are not sufficiently acidic to ionize appreciably at a pH below 7. Furthermore, the functional groups of organic matter in acid soils are believed to be countered by Al and Fe which are not readily exchanged by neutral salts (Schnitzer and Skinner, 1963; Mortensen, 1963). The work of McLean et al. (1965) and of Sawhney et al. (1970) indicated that weakly dissociated acid groups of organic matter contribute significantly to the pH-dependent CEC and thus to the titratable (or pH-dependent) acidity.

In general, little or no importance is attached to the exchange acidity for practical purposes in fertility work. However, some authors (Kamprath, 1970; Reeve and Sumner, 1970) suggested that lime applications in Ultisols and Oxisols based on exchangeable Al would be a realistic approach.

There is still considerable disagreement concerning the methods for the determination of exchange acidity. Titrations, both conducto-metric and potentiometric, have been used for many years to charac-terize soil acidity in strength and amounts (Lin and Coleman, 1961; Volk and Jackson, 1964; Dewan and Rich, 1970). The most widely used method to measure the exchange acidity is leaching with $\underline{N}$ KCl (Lin and Coleman, 1961). Other workers (McLean et al., 1959) favored extraction with $\underline{N}$ NH_4OAc buffered at pH 4.8. Pratt and Bair (1961) found that, relative to unbuffered, neutral salts, $\underline{N}$ NH_4 OAc extracted less Al from soils of lower pH, and more Al from soils of higher pH; they concluded that KCl gives a more reliable estimate of exchangeable Al.

Titrimetric methods have often been used in conjunction with neutral salt extractions. Lin and Coleman (1961) found good agreement between titrimetrically determined and salt exchangeable acidity in subsoil samples low in organic matter, whereas in other soils, con-taining mostly kaolin and Fe oxides, the titrated acidity was signifi-cantly larger than the amount of Al displaced by KCl. The extraction

method used by Dewan and Rich (1970) is much more exhaustive and undoubtedly furnishes higher results than the classical methods. In their very careful titrimetric study on samples of varied mineralogy, these authors obtained relatively consistent results from KCl extractions, potentiometric titrations in KCl, and conductometric titrations, if in the latter method corrections were made for the aluminate reaction and a base was used that efficiently displaces Al (e.g., $Ba(OH)_2$). Dewan and Rich (1970) also reported that in subsoil samples low in organic matter most of the exchange acidity is removed in the first few extractions, but that the release in samples high in organic matter is slower.

Skeen and Sumner (1965) asserted that there is no satisfactory quantitative method to determine exchange acidity. They proposed a method by which soils were repeatedly extracted with 0.2 $\underline{N}$ KCl or NH_4Cl adjusted to the pH of the soil. The assumption is made that the amount of non-exchangeable Al dissolved during each extraction is constant, and therefore the sum of the contributions of this source can be subtracted from the total exchangeable Al. No comparisons with other methods were made.

Fe and Al in Organo-Mineral Interactions

Knowledge about the chemical nature of the wide range of organic compounds occurring in soils is still very limited. The broad classification scheme of humified organic materials into humins (not extractable by alkali), humic acid (alkali soluble and precipitated by acids), and fulvic acid (alkali soluble and not precipitated by acids) is still commonly used.

Humic acids are presumably composed of amino acids and phenolic compounds to form a group of high molecular weight polymers. Fulvic acids contain phenolic materials probably similar to humic acids but of lower molecular weight; they also include a group of polysaccharides besides other materials (Greenland, 1965b). Mehta et al. (1963) using gel filtration on Sephadex have reported average molecular weights for fulvic acid (3000) and humic acid (25,000) from a Podzol, and a total range of molecular weights ranging from 2000 to over 200,000. Similar results were obtained by Posner (1963), whereas Schnitzer and Desjardins (1962) using a cryoscopic method reported a much lower value for a Podzol fulvic acid. Functional group analysis has shown the presence of carboxyl, phenolic and alcoholic hydroxyl, carbonyl, and methoxyl groups (Burges, 1960; Wright and Schnitzer, 1960; Lewis and Broadbent, 1961; Schnitzer and Skinner, 1965; Riffaldi and Schnitzer, 1972);

the relative proportion of these functional groups varies with soil type, horizon, and method of isolation of the fraction.

Products resulting from the interaction of organic materials with inorganic soil constituents such as metal ions, hydrous oxides, and clay minerals are likely to affect soil properties. Research in this field is difficult, not only because there are many uncertainties regarding the chemical nature of organic matter, but also because little is known about the nature of the inorganic surfaces at which the interaction occurs, particularly in the case of the amorphous oxides and hydroxides of silicon, aluminum and iron. The recognition of the existence of organo-mineral compounds goes back to Meyer (1935). He appears to have been the first worker to suspect the adsorption of alkali-soluble products of humification by clays, and he proposed the use of such complexes to improve the nutritional potential of soils. Later, Bremner et al. (1946) suggested that polyvalent cations in soils exist as insoluble organo-metallic complexes. This led to numerous studies concerned with interactions of metal ions and clays with soil organic matter.

Evidence for chelation or complexing of metals by organic matter has been based on the ability of soil to retain certain cations adsorbed from solution. Thus it was found that copper retention by soils is correlated with organic matter and pH (Tobia and Hanna, 1958; Northmore, 1959). Bloomfield (1956), and Schnitzer and DeLong (1956)

showed that aqueous leaf extracts are capable of dissolving ferric and aluminous oxides. The ability of chelating agents, such as neutral pyrophosphate, to extract organic matter from soils has been attributed to the complexing of metals with concommitent solubilization of organic matter (Bremner et al., 1946; Bremner and Lees, 1949).

Deb (1949) and Martin and Reeve (1960) showed that mutual coagulation and peptization occurs when organic matter extracts are mixed with Al or Fe ions or their hydroxides. These reactions were markedly influenced by pH and the ratio of carbon to metal. Schnitzer and Skinner (1965) concluded that acidic COOH and phenolic OH groups were the only functional groups of a Podzol fulvic acid involved in the interaction with metal ions. Schnitzer and Skinner (1964) compared metal-fulvic complexes in the laboratory with an untreated organic matter extract from a Podzol Bh horizon, and showed their chemical, spectroscopic and thermogravimetric properties to be very similar. In further work Schnitzer and Hanson (1970) studied the stability constants of metal-fulvic acid complexes and reported decreasing stability constants at low pH in the order Fe, Al, Cu, Ni, Co, Pb, Ca, Zn, Mn, Mg. No similarly thorough studies have been made with humic acids.

Another approach frequently used in studying organo-mineral interactions is concerned with the adsorption of either defined organic compounds or of soil organic compounds by clay minerals.

It has been shown that larger amounts of organic matter are adsorbed by clay when Fe and Al are present on the exchange sites (Sen, 1960; Evans and Russel, 1959; Scharpenseel, 1966 and 1968). Humic and fulvic acids are also readily adsorbed by freshly precipitated Fe and Al oxides (Aleksandrova and Nad, 1958; Evans and Russel, 1959; Martin and Reeve, 1960; Levashkevitch, 1966; Scharpenseel, 1966 and 1968). There is some disagreement concerning the linking ability of different inorganic compounds. Evans and Russel (1959) found Ca^{++} and Mg^{++} equally efficient in a humic acid-bentonite system; they also reported different linking abilities for cations on kaolinite. Scharpenseel (1966 and 1968), using a radiometric method, reported that while H^+, Na^+, K^+, Mg^{++} did not specifically stimulate the production of clay-organic complexes, NH_4^+, Al^{3+}, Ca^{++}, Fe^{3+}, in this order, acted increasingly as bridging cations in a montmorillonite-humic (fulvic) acid system. However, he found no evidence for such effects in a kaolinite system. In agreement with Aleksandrova and Nad (1958), Scharpenseel (1966) noted that amorphous forms of Fe oxides have a greater capability of binding organic matter than crystalline forms. Freshly precipitated Al hydroxides appear to adsorb more organic matter than the Fe hydroxides and are more stable (Levashkevich, 1966). Inoue and Wada (1968) studied the adsorption of aqueous extracts of humified clover on various clays. The adsorption of organic matter on allophane (Si/Al less than 1/1. 5)

was roughly eight times higher than on montmorillonite, and neither the exchangeable cations (Ca, Al) of the clay nor the presence of extractable Fe oxides affected the differences in the extent of adsorption. A marked preferential adsorption of darker colored components with higher molecular weight was observed for allophane. Schnitzer and Kodama (1966) have shown that fulvic acid is adsorbed in the inter-lamellar spaces of montmorillonite only at low pH.

Some attempts have been made to determine the proportion of soil organic matter contained in the clay-organic complex. The method used for the separation consists generally of a dispersion followed by a flotation of the free organic material in a liquid of density intermediate to that of the free material and the clay-organic complex. Values reported for the proportion of soil carbon in the clay-organic complex in Rendzinas are around 66% (Henin and Turc, 1950; Greenland and Ford, 1964), 90% in a Podzol (Khan, 1959), 98% in a Lateritic Red Earth (Greenland and Ford, 1964). All these workers also noted that the free material is in a much earlier stage of decomposition than the combined material.

In recent reviews (Greenland, 1965a, 1965b, 1971; Mortland, 1970), several mechanisms of bonding between organic matter and inorganic soil materials have been considered. Most of the organic matter in soils is present as negatively charged polymeric material; hence, it can enter coulombic interactions. This occurs in anion-

exchange adsorption (Greenland, 1971) of organic anions on hydrous

oxides which have positive sites below pH 8. Coulombic forces also

cause bonding of organic anions through polyvalent cation bridges to

negative sites on lattice clays. A similar mechanism can be inferred

for allophane.

Metallic cations, with their associated water, may also serve

as adsorption sites for polar, non-ionic molecules by ion-dipole or

coordination type of interactions (Mortland, 1970). Hydrogen bonding

occurs in water bridges linking both polar molecules and organic

anions to exchangeable cations or other positively charged sites;

hydrogen bonding directly links organic molecules to the silanol sur-

faces of mica-type clays (Greenland, 1971; Mortland, 1970). At lower

water contents, organic molecules and clays can come into sufficiently

intimate contact so that van der Waals forces become significant. Both

hydrogen bonds and van der Waals forces are relatively weak, but due

to their additivity, they appear to be significant in the case of large

molecules and polymers (Mortland, 1970). The adsorption of some

organic molecules seems to be favored if there is a positive entropy

change in the system due to the desorption of several water molecules.

The work of Hingston et al. (1967) has shown that in the case of

hydrous Fe and Al oxides, ligand exchange (also called specific ad-

sorption) normally occurs. In this type of linkage the anion penetrates

the coordination shell of an Al or Fe atom, and is thus incorporated

in the surface of the oxide. Maximum adsorption of this type takes place when the pH of the system equals the pK value of the functional group involved (Greenland, 1971).

Edwards and Bremner (1967a, 1967b) have attempted to relate bonding mechanisms to aggregate formation and stability. In the view of these authors, clay particles bonded to humified organic material by polyvalent metal cations (C-P-OM) aggregate into larger $(C-P-OM)_x$ and still larger $((C-P-OM)_x)_y$ units, the latter ones representing microaggregates (250μ diameter). The aggregation is presumably largely a result of the bridging of polyvalent ions, although other types of linkages are not excluded. According to Edwards and Bremner (1967a), the bonds linking C-P-OM units into microaggregates are relatively weak, and can be disrupted by simple mechanical means such as sonic or ultrasonic vibrations, or prolonged shaking in water.

Organo-mineral interactions have important implications with regard to the biological stability of organic matter in soils. In general, close relationships between organic matter and clay contents in soils can be observed. Resistance of organic matter against microbial attack as a result of organo-mineral interactions has been attributed to several mechanisms. Protection has been ascribed to the adsorption of organic matter on clay minerals, and to the adsorption and inactivation of attacking enzymes (Ensminger and Gieseking, 1942; Mortland and Gieseking, 1952). Montmorillonitic clays have been

found to have a greater protective effect than other minerals tested. Kaolinite appeared to have little protective effect or even a stimulating effect (Esterman and McLaren, 1959). Organic matter contained in very fine pores may be inaccessible to bacteria (Rovira and Greacen, 1957), although this would not protect against exoenzymes, and in addition, this would also depend on the extent to which soil is worked by the soil fauna (Greenland, 1965b). Mutatkar and Pritchett (1966) have suggested that Al may have toxic effects on microbial activity.

Jenny (1961b) noted that the levels of organic matter in Latosols are often greater than predicted from climatic relationships derived for temperate soils. High levels of organic matter and slow minerali- zation of N and C in allophanic soils in New Zealand were reported by Broadbent et al. (1964). Kawaguchi and Kyume (1959) have related the humus accumulation to the large amounts of Al found in these soils. Both ionic and polymeric forms of Al appear to be of paramount im- portance in the accumulation of organic matter in allophanic soils.

Biological stability can also be related to the resistance to de- composition exhibited by certain components of organic matter, such as compounds resulting from reactions between nitrogenous compounds with lignin (Bremner, 1967).

From the multitude of organo-mineral interactions in soils it is obvious that reasonably complete soil characterization work would have to rely on many different determinations.

Most quantitative methods proposed so far have been aimed at the portion of the organic matter that is linked to the inorganic fraction predominantly by polyvalent cation bridges. This dates back to Bremner et al. (1946) and Bremner and Lees (1949) who compared the ability of different neutral chelating agents to extract organic matter. Sodium pyrophosphate proved to be the most efficient, and it was concluded that the organic matter extracted by it was associated with polyvalent cations. The idea was brought up again by Aleksandrova (1960) who postulated that Na-pyrophosphate at its natural pH of about ten is specific for humic substances and their complex Al and Fe salts. The specificity of Na pyrophosphate for organically bonded Al and Fe has been denied by many workers (Titova, 1962; Kononova et al., 1964; Bascomb, 1968; Grimme and Wiechmann, 1969; Duchaufour, 1964). some of whom showed that pyrophosphate is able to dissolve inorganic forms of Fe and Al. Other researchers have supported the method and modified it to increase its specificity (McKeague, 1967; Bascomb, 1968; Flach et al., 1969). Posner et al. (1968) have reported that humic acids extracted with pyrophosphate were in the greatest state of oxidation with the least resemblance to lignin. Still other workers (Duchaufour, 1964; Grimme and Wiechmann, 1969) have proposed different methods based on Na-hydroxide. Regardless of the specificity of Na pyrophosphate for organically bound Fe and Al, it appears to be a useful method in soil characterization work and has been widely adopted (McKeague, 1968; Soil Survey Staff, 1970).

Pedogenetic Oxides

Hydroxides and oxides of Fe and Al are weathering products in many soils. The formation of these oxides depends on the weathering conditions and on the parent material. In soils that are subject to strong weathering and leaching, the silicic acid is usually depleted more rapidly than Al and Fe. The result is an accumulation of amorphous hydrous oxides of Al and Fe. Under more moderate conditions, the formation of silicate clay minerals together with hydrous oxides may be dominant (Schwertmann, 1966). As mentioned earlier, these newly formed materials affect many soil properties by forming interlayers and coatings, and by their interaction with organic matter. Where concretions are absent, the hydrous oxides are concentrated in the clay fraction (Oades, 1963). The extent of formation of hydrous oxides, as well as further transformations, such as movement and reprecipitation, or the formation of crystalline forms through aging, makes these materials, particularly the various forms of Fe useful indicators in soil genesis and classification (Gorbunov et al., 1961; Mitchell et al., 1964). However, specific knowledge on their formation and the forms resulting from aging is still somewhat limited. It is only in recent years that attempts to quantitatively distinguish different forms have been made.

The first step in the formation of Al and Fe oxides is the liberation of ionic forms of these elements by weathering of primary

minerals. In the following transformations which follow, Fe and Al appear to behave somewhat differently.

Ferric ions in soils are hydrolytically precipitated in situ or after transportation as hydrous oxides (Oades, 1963). Further transformations depend mainly on pH, temperature, redox potentials, and the presence of other compounds. Schwertmann et al. (1964) have shown that the crystallization of artificial and natural ferric hydroxides is significantly retarded or even inhibited by organic compounds; the strongly pH-dependent character of this interaction led these authors to conclude that functional groups of organic anions can successfully compete with OH^- for adsorption sites and thus inhibit crystallization.

The Fe oxides most commonly encountered in soils are goethite (α-FeOOH) and hematite (α-Fe$_2$O$_3$), to a lesser extent lepidocrocite and maghemite. Goethite is the predominant form of the temperate humid climate. Its formation in soils is generally attributed to at least two different processes (Schwertmann, 1959a; Oades, 1963): (1) direct slow precipitation of ferric ions in solution at low pH, and (2) aging of ferric hydroxide gel. Low temperature, high pH, and the presence of various ions, particularly SO_4^{--} and HCO_3^-, favor the formation of goethite (Schellmann, 1959). The proportion of goethite and its degree of crystallization increases with age.

The formation of hematite, in contrast, is favored by high temperature and low pH (Schellmann, 1959). According to Oades (1963), all Fe oxides can artificially be transformed to hematite when heated to sufficiently high temperatures, but Schwertmann (1966) discounts the possibility of hematite formation by dehydration of goethite in soils. Hematite is more commonly found in subtropical and tropical soils. Once formed, hematite is very stable (Schwertmann, 1966); red soils containing hematite and occurring presently in the temperate humid climate (e.g., Germany) are considered to be fossil formations.

The orange colored lepidocrocite is an Fe oxide that typically forms in waterlogged soils, often together with goethite (Brown, 1953).

In soils of the temperate humid climate, the free Al oxide content is generally low. In such climates Al normally participates either in the formation of clay minerals, or it forms gibbsitic interlayers in expandible layer silicates (Schwertmann, 1966). It has been suggested that Al oxides have a specific affinity for silica in solution (Mitchell et al., 1964). Rich and Thomas (1960) have proposed that the lack of free amorphous Al in soils may be due to its stabilization by silica in allophane. Free Al oxides attain a maximum concentration in highly leached tropical soils where they are generally present in the form of gibbsite and boehmite (Alexander et al., 1956). Determinations of various forms of pedogenetic oxides are potentially very useful

in studies of soil genesis and classification, but the methods that have been proposed are still quite inadequate.

Various methods based on Na-dithionite have been used for many years to determine free iron oxides. The method proposed by Mehra and Jackson (1960) has gained general acceptance. Both amorphous and crystalline oxides of Fe are extracted by this method. However, some structural Fe is extracted from Fe-bearing silicate minerals such as nontronite (Dudas and Harward, 1971). Since iron oxides can also be inherited from the parent material, such determinations are strictly valid only for comparison of horizons within the same profile, of for soils formed on the same parent material.

Schwertmann (1959a, 1964) retested acid ammonium oxalate (Tamm's reagent) as an extractant for pedogenic oxides and claimed that it selectively dissolves amorphous forms of Fe. This was confirmed by McKeague and Day (1966). However, Baril and Bitton (1969) showed that acid oxalate is able to dissolve magnetite. In a recent paper, Pawluk (1972) claimed that oxalate extracts more Fe than dithionite but at a much slower rate. He concluded, however, that the amount of Fe obtained in two oxalate extractions probably serves as a fairly good indicator of the relative amounts of amorphous Fe oxides, but he doubts whether these values can be used as specific criteria in soil classification.

MATERIALS AND METHODS

Soils

Five coastal Inceptisols were selected for this study. In addition, a Mollisol from the Willamette Valley, and an Ultisol were included for comparative purposes.

All the coastal soils were sampled within a fairly restricted area of central-western Tillamook County. The climate of the area is characterized by high winter rainfall, mild winters, and relatively dry and cool summers. The annual rainfall is 240 cm, half of which falls during winter. Mean monthly temperatures range from $4.4^{\circ}C$ in winter to a maximum of about $15.5^{\circ}C$ in summer (Bowlsby and Swanson, 1964).

In the following profile descriptions colors are given for moist conditions, and the pH was determined with dye indicators, except for the Woodburn soil, where the field pH was not determined.

Quillayute Silt Loam

Location: SW 1/4, NW 1/4, Sec. 13, T. 1S., R. 10 W., 110' north of farm road, 100' east of point where road joins Wilson River. Sampling and Description: E.G. Knox and G. Spycher, June 23, 1971. Parent material: Old alluvium from mixed igneous and sedimentary rocks on river terrace.

Soil surface: 2% slope, non-stony.

Drainage: well drained, moist when sampled.

Vegetation: Grass, clover.

Classification, Thixotropic, mesic, Typic Dystrandept.

Horizon	Depth	Description
Alp	0-20 cm	Black (10YR2/1) silt loam; moderate fine and very fine subangular blocky structure that breaks to strong very fine granular structure; friable, slightly sticky, slightly plastic; many roots, many very fine tubular and interstitial pores; medium acid (pH 5.6); clear smooth boundary.
A12	20-48 cm	Black (10YR2/1) silt loam; weak fine and very fine subangular blocky structure that breaks to strong very fine granular structure; friable, slightly sticky, slightly plastic; many roots; many fine tubular and interstitial pores; very strongly acid (pH 5.0); clear wavy boundary.
A31	48-63 cm	Black (10YR2/1) silty clay loam; weak fine and very fine subangular blocky structure that breaks to strong very fine granular structure; friable, sticky, plastic; many roots; many very fine tubular pores; strongly acid (pH 5.2); gradual smooth boundary.
A32	63-83 cm	Very dark grayish brown (10YR3/2) silty clay loam; weak very fine subangular blocky structure; friable, sticky, plastic; common roots; many very fine tubular pores; strongly acid (pH 5.2); clear wavy boundary.
B2	83-110+ cm	Dark yellowish brown (10YR4/4) silty clay loam; moderate very fine and weak fine subangular blocky structure; friable, sticky, plastic; few roots; many very fine tubular pores; strongly acid (pH 5.4).

Hembre Silt Loam

Location: SW1/4, NE1/4, Sec. 14, T. 2 S., R. 9 W.

Sampling and description: R. T. Meurisse (1970).

Elevation: 106 m.

Soil surface: Uneven-dissected slope.

Classification: Typic Dystrandept.

Horizon	Depth (cm)	Description
01	12-7	Fresh mat of leaves, twigs and moss; extremely acid (pH 4.3)
02	7-0	Partly decomposed needles, leaves, twigs, and bark mixing with mineral soil; extremely acid (pH 4.0)
A1	0-18	Dark reddish brown (5YR 3/2 moist) silt loam; moderate fine, medium and coarse subangular blocky and moderate medium granular structure; slightly hard, friable, slightly sticky and slightly plastic; abundant very fine, medium and common fine roots; very strongly acid (pH 4.8); clear wavy boundary. (10 to 25 cm thick)
B21	18-51	Dark reddish brown (5YR 3/3 moist) light silty clay loam; strong very fine, fine, and medium granular structure; slightly hard, friable, slightly sticky and slightly plastic; very few very fine and fine and few medium and coarse roots; very strongly acid (pH 5.0); clear wavy boundary. (25 to 35 cm thick)
B22	51-99	Yellowish red (5YR 4/6 moist) silty clay loam; moderate very fine and fine subangular blocky structure; slightly hard, friable, sticky and slightly plastic; very few very fine and fine roots; strongly acid (pH 5.2); clear wavy boundary. (45 to 55 cm thick)

Horizon	Depth (cm)	Description
B3	99-132	Reddish brown (5YR 4/4 moist) clay loam or silty clay loam; weak very fine and fine subangular blocky structure; hard, firm, sticky and slightly plastic; very few very fine and fine roots; very strongly acid (pH 4.8); clear wavy boundary. (25 to 35 cm thick)
C	132-234	Reddish brown (5YR 4/4 moist) clay loam or silty clay loam; massive; hard, firm, sticky and slightly plastic; very few and very fine and fine roots; very strongly acid (pH 4.8).

Hembre Silt Loam

Location: SE1/4, SW1/4, Sec. 17, T. 2S. R. 9 W.

Sampling and description: R. T. Meurisse (1970).

Elevation: 778 m.

Soil surface: Smooth slope.

Classification: Typic Dystrandept.

Horizon	Depth (cm)	Description
01	2-0	Raw leaves, twigs, and bark.
A1	0-10	Black (N2/moist) silt loam; moderate very fine and fine granular structure; soft, very friable, slightly sticky and slightly plastic; common very fine and few fine and medium roots; ten percent fine gravel; very strongly acid (pH 5.0); clear smooth boundary. (5 to 15 cm thick)
B21	10-33	Black (7.5YR 3/2 moist) gravelly silty clay loam; moderate medium subangular blocky structure; slightly hard, friable, slightly sticky and slightly plastic; common fine and few very fine, medium and coarse roots; 20 percent fine gravel; extremely acid (pH 4.4); clear smooth boundary. (15 to 30 cm thick)

Horizon	Depth (cm)	Description
B22	33-51	Dark brown (7.5YR 3/2 moist) gravelly silty clay loam; weak medium subangular blocky structure; slightly hard, friable, slightly sticky and slightly plastic; 30 percent fine gravel; very strongly acid (pH 4.6); gradual wavy boundary. (15 to 25 cm thick)
B3	51-81	Brown to dark brown (7.5YR 4/2 and 7.5YR 3/2 moist) gravelly silt loam; massive or weak medium and coarse subangular blocky structure; slightly hard, friable, slightly sticky and slightly plastic; few very fine and fine roots; 35 percent fine gravel; very strongly acid (pH 4.8); gradual irregular boundary. (20 to 35 cm thick)
C	81-122	Brown to dark brown (7.5YR 4/2 and 7.5YR 3/2 moist) gravelly silt loam; massive; slightly hard, friable, slightly sticky and slightly plastic; few very fine and fine roots; 50 percent fine gravel; very strongly acid (pH 5.0); clear wavy boundary. (35 to 50 cm thick)
R	122[+]	Fractured basalt rock.

Knappa Silt Loam

Location: NW1/4, NW1/4, Sec. 21, T.2 S., R. 9 W., west of highway U.S. 101. 25' from cut bank, 100' south of field boundary.

Sampling and description: E.G. Knox and G. Spycher, June 23, 1971.

Parent material: Old alluvium from mixed igneous and sedimentary rocks on river terrace.

Soil surface: 2% slope, non-stony.

Drainage: well drained, moist when sampled.

Vegetation: Grass, bracken, other weeds (idle area cut off by highway).

Classification: Fine-silty, mixed, mesic Typic Dystrandept.

Horizon	Depth (cm)	Description
A11	0-20	Very dark brown (10YR 3/3) silt loam; moderate very fine subangular blocky structure that breaks to strong very fine granular structure; friable slightly sticky, slightly plastic; many roots; many very fine interstitial pores; slightly darker (10YR 2/3) coatings on ped surfaces; very strongly acid (pH 5.0); clear smooth boundary.
A12	20-50	Dark brown (10YR 3/3) silt loam; weak fine and very fine subangular blocky structure that breaks to moderate very fine granular structure; friable, slightly sticky, slightly plastic; common roots; many very fine tubular pores; very strongly acid (pH 5.0); clear smooth boundary.
B21	50-85	Dark yellowish brown (10YR 4/4) silt loam; moderate fine and very fine subangular blocky structure; friable, slightly sticky, slightly plastic; few roots; many very fine tubular pores; slightly darker coatings (10YR 4/3) on ped surfaces; very strongly acid (pH 5.0); gradual smooth boundary.
B22	85-105	Dark yellowish brown (10YR 4/4) silt loam; moderate very fine and fine subangular blocky structure; friable, slightly sticky, slightly plastic; few roots; many very fine tubular pores; slightly darker (10YR 4/3) coatings on peds; few faint mottles; very strongly acid (pH 5.0).

Nehalem Silt Loam

Location: SW1/4, SW1/4, Sec. 34, T. 1S., R. 9W. 150' west of road, 135' south of driveway.

Sampling and description: E. G. Knox and G. Spycher, June 23, 1971.

Parent material: Alluvium from igneous and sedimentary rocks on floodplain.

Soil surface: 1% slope, non-stony.

Drainage: Well drained, moist when sampled.

Vegetation: Grass and clover.

Classification: Fine-silty, mixed mesic, Fluventic Hapludoll.

Horizon	Depth (cm)	Description
Ap	0-20	Dark brown (10YR 3/3) silt loam; strong fine and very fine subangular blocky structure; friable; slightly sticky, slightly plastic; many roots; many very fine interstitial pores; slightly darker colored coats on ped surfaces; medium acid (pH 5.6); clear smooth boundary.
B21	20-38	Dark brown (10YR 3/3) silt loam; weak fine and very fine subangular blocky structure that parts to moderate very fine granular structure; friable, slightly sticky, slightly plastic; many roots, many very fine tubular pores; medium acid (pH 6.0); clear smooth boundary.
B22	38-62	Dark brown (10YR 3/3) silt loam; strong fine and very fine subangular blocky structure; friable, slightly sticky; slightly plastic; many roots; many very fine tubular pores; slightly darker colored coats on ped surfaces; slightly acid (pH 6.2); gradual wavy boundary.
B23	62-100	Dark brown (10YR 4/3) silt loam; moderate fine and very fine subangular blocky structure; friable, slightly sticky, slightly plastic; common roots; many very fine tubular pores; slightly acid (pH 6.2).

Woodburn Silt Loam

Location: NW1/4, NW1/4, Sec. 9, T. 11 S., R. 4 W., Hyslop

Agronomy Experimental Farm.

Sampling and description: E. G. Knox and G. Spycher, Oct. 27, 1971.

Parent material: Silty alluvial deposit.

Soil surface 1% slope.

Drainage: moderately well drained.

Vegetation: cultivated field.

Classification: Fine-silty, mixed, mesic Aquultic Argixeroll.

Horizon	Depth (cm)	Description
Ap	0-24	Very dark brown (10YR 2/2) silt loam; moderate very fine subangular blocky structure; friable, slightly sticky, slightly plastic; many roots; many very fine and few medium and coarse tubular pores; slightly acid; abrupt smooth boundary.
A12	24-42	Dark brown (10YR 2/2) silty clay loam; moderate fine and very fine subangular blocky structure; friable, sticky, plastic; many roots; many very fine and few medium tubular pores; slightly acid; clear smooth boundary.
B1	42-62	Dark brown (10YR 3/3) silty clay loam; moderate fine subangular blocky structure that parts to weak very fine subangular blocky structure; friable, sticky, plastic common roots; many very fine and few medium and coarse tubular pores; few mottles; few scattered thin clay skins; slightly acid; clear smooth boundary.

Horizon	Depth (cm)	Description
B2t	62-95	Dark yellowish brown (10YR 4/4) silty clay loam; moderate very coarse prismatic structure that parts to moderate coarse subangular blocky structure; firm, sticky, plastic; common roots; few medium tubular pores; common very fine tubular pores; prominent medium clay skins; common medium distinct mottles, dark yellowish brown (10YR 3/4) when moist; slightly acid; gradual smooth boundary.
B3t	95-125	Yellowish brown (10YR 5/4) silty clay; weak very coarse prismatic structure that breaks to weak very coarse subangular blocky structure; firm, sticky, plastic; few roots; few medium, and common very fine tubular pores; prominent medium clay skins; slightly acid.

Jory Clay Loam

Sample number: S55Ore -2-2-1 through 7.

Location: Benton County, Oregon. SE corner of Sec. 4, T. 11 S., R. 5 W. in the McDonald Forest, about 300 feet SE of the road intersection at Lewisberg Saddle.

Sampling: Originally sampled as Aiken clay loam by R. C. Roberts, J. M. Williams, J. S. Allen, and E. G. Knox, November 5, 1955.

Resampled by J. A. Norgren and G. Spycher, October, 1971.

Classification: Clayey, mixed, mesic Xeric Haplohumult.

Description: E. G. Knox.

Parent material: Residuum from basalt.

Vegetation at the time of sampling: The area had been logged. At

the time of sampling the vegetation included grass, blackberry, poison oak, fern, young Douglas-fir, hazel nut, madrone, bigleaf maple, dogwood, and thimbleberry.

Physiography and relief: The sample site is on a 15% northwest slope in hilly upland.

Elevation: 1000 feet.

Stoniness: non-stony.

Moisture condition at the time of sampling: moist.

Horizon	Depth (cm)	Description
A1	0-10	Dark reddish brown (5YR 3/3 dry, 5YR 2/2 moist), clay loam; strong medium to very fine granular structure; very friable, slightly sticky, slightly plastic; common fine spherical pellets (shot) in the top inch, few below; abundant roots; pH 6.0 (Chlorphenol red); lower boundary smooth and clear.
A3	10-22	Dark reddish brown (5YR 3/2 dry, 5YR 2/2, moist) clay loam; strong medium subangular blocky breaking to moderate fine and very fine subangular blocky breaking to moderate fine granular structure; friable, slightly sticky, slightly plastic; few fine spherical pellets; abundant roots; lower boundary smooth and clear.
B1	22-35	Reddish brown (4YR 4/3, dry), dark reddish brown (4YR 3/3, moist) clay; strong fine and very fine angular blocky structure; friable, sticky, plastic; thin continuous clay flows; common roots; a few old root channels filled with material from above; pH 5.8 (chlorphenol red); lower boundary smooth and clear.

Horizon	Depth (cm)	Description
B21	35-51	Reddish brown (2.5YR 4/4, dry), dark reddish brown (2.5YR 3/4, moist) clay; moderate fine and very fine angular blocky structure; friable, plastic, sticky; thin continuous clay flows, roots common; pH 5.6 (chlorphenol red); lower boundary smooth and gradual.
B22	51-29	Reddish brown (2.5YR 4/4, dry) dark reddish brown (2.5YR 3/4, moist) clay; moderate fine angular blocky structure; friable, sticky, plastic; thin continuous clay flows; common roots; pH 5.4 (chlorphenol red); lower boundary smooth and gradual.
B3	72-110	Red (2.5YR 4/6, dry), dark reddish brown (2.5YR 3/4, moist) clay; moderate medium and fine angular blocky structure; friable, sticky, plastic; thin continuous clay flows; few black (MnO_2) splotches; few basalt fragments; few roots; pH 5.4 (chlorphenol red); lower boundary smooth and gradual.
B3 Dr	110-130	Red (2.5YR 4/8, dry), dark red (2.5YR 3/6, moist) clay; moderate medium and fine angular blocky structure; friable, slightly plastic, slightly sticky; common thin patchy clay flows; abundant basalt fragments (about 50% by volume); pH 5.4 (chlorphenol red).

Methods

Routine Soil Characterization Methods

All soil samples were air dried, crushed, and passed through a 2 mm sieve.

The soil reaction was determined in 1:1 soil-water, and in 1:1 soil-$\underline{N}$ KCl suspensions using a Corning Model 7 pH meter. The pH values in 1:50 soil-NaF suspension were determined according to the method of Fieldes and Perrot (1966).

Exchangeable bases (Ca, Mg, K) were extracted with $\underline{N}$ NH_4OAc at pH 7 (Peech et al., 1947), and determined on a Perkin Elmer Atomic Absorption unit. Buffered $\underline{N}$ NH_4OAc was also used to determine the CEC at pH 7 (Schollenberger and Simon, 1945).

The neutral salt CEC was measured by a method used by DeVilliers and Jackson (1967). Ten grams of soil were equilibrated four times with 25 ml of 0.5 $\underline{N}$ $CaCl_2$ for 20 minutes on a reciprocating shaker. The Ca-saturated soil was washed free of excess salt with four water washes. Ca was exchanged by four washes with 25ml of 0.5 $\underline{N}$ $MgCl_2$ after 20 minutes of shaking. Calcium was determined on a Perkin Elmer Atomic Absorption unit.

Oxidizable carbon was measured by the Walkley-Black wet digestion procedure (Walkley, 1946), and converted to organic carbon using a factor of 1.33.

On the Knappa samples, the moisture retention at 15 bars pressure was determined with a standard pressure plate apparatus. The clay content of these samples was measured with the pipette method (Kilmer and Alexander, 1949).

All analyses was conducted in duplicate.

Exchangeable Aluminum

A modified version of the method of Dewan and Rich (1970) was used to determine exchangeable Al. Duplicate samples of 10 g of air-dry, 2 mm soil were placed into extraction columns, one inch in diameter. The soil was continuously leached with $\underline{N}$ KCl. The flow rate was adjusted to 100 ml/hour by means of a screw compressor clamp below the column. Eight portions of 50 ml were collected from each leaching operation. The exchange acidity was determined by titrating an aliquot of 20 ml to pH 8 with 0.1 $\underline{N}$ NaOH. The high pH was chosen to overcome a small depressing effect of chloride ions on the endpoint (Rich, 1970).

Twenty ml of $\underline{N}$ KCl were titrated as a blank and corrections made. The Al in the leachates was measured colorimetrically using the aluminon reagent (Hsu, 1963). Two ml of 1% thioglycolic acid were added prior to the color development to eliminate the interference of iron. Colorimetric measurements were made with a Bausch-Lomb Spectronic 20 spectrophotometer.

Fe and Al in Organic Matter

Organically bound Al and Fe were extracted with Na-pyrophos-phate (McKeague, 1968). Duplicate 4 g soil samples were shaken for 16 hours in 200 ml of 0.1 M $Na_4P_2O_7$ at its natural pH of ten. The soil suspensions were centrifuged for 20 minutes at 10,000 rpm, and the supernatant solutions decanted into beakers. The extracts were acidified to pH 2 with 6 $\underline{N}$ H_2SO_4, allowed to stand overnight, and then centrifuged. The centrifugate (fulvic acid) was decanted and the vol-ume measured. The residue (humic acid) was dissolved and diluted to 50 ml with $\underline{N}$ NaOH. The Fe and Al content of the humic and fulvic acid were determined with atomic absorption techniques. Oxidizable carbon was measured by dichromate oxidation (Walkley, 1946). The ratio of water:H_2SO_4 is an important factor in the digestion process of organic matter. Since the humic and fulvic acid preparations were added in liquid form, equivalent amounts of sulfuric acid were added to maintain the recommended 2:1 ratio of acid to water.

Pedogenetic Oxides

In an attempt to differentiate amorphous from crystalline oxides of Fe, ammonium oxalate and dithionite-citrate-bicarbonate were used respectively.

Duplicate air-dry soil samples, 2.5 g, were extracted with 100 ml of ammonium oxalate adjusted to pH 3 with oxalic acid (McKeague

and Day, 1966). The extraction units were shaken for four hours in the dark. The suspensions were centrifuged until clear, and aliquots were saved for Fe and Al analyses.

Samples of 4 g of air-dry soil were extracted twice by the di-thionite-citrate-bicarbonate procedure of Mehra and Jackson (1960), followed by two washings with Na-citrate. The extracts and the washings were combined and made to volume.

Fe and Al in both extracts were determined on a model 306 Perkin Elmer Atomic Absorption unit (Road et al., 1966).

RESULTS AND DISCUSSION

General Chemical Characteristics

All of the coastal soils are medium to extremely acid (Table 1).
The lowest pH values were measured in the two Hembre soils. These
two soils also exhibit the least difference between H_2O- and KCl-
values, particularly in the top horizons. No satisfactory explanation
could be found for this; the type of organic matter present in these
soils is possibly involved. The pH values (H_2O) of Woodburn and Jory
are somewhat higher than in coastal soils, but their pH values (KCl)
are similar to those found in coastal soils. These modest differences
are in sharp contrast to the very low base saturation in the coastal
soils (except Nehalem) compared to Woodburn and Jory. Relatively
high pH at low base saturation is characteristic for soils whose
properties are influenced by allophanic materials (Fieldes and Scho-
field, 1960). The presence of considerable amounts of amorphous
aluminosilicates has been shown in similar soils, including samples
of the Quillayute series by Franklin (1970), and by Meurisse (1972)
for the two Hembre profiles used in this study.

The data in Table 1 will be further discussed in later sections.

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Table 1. Chemical properties of the soil samples.

Soil and Horizon	pH (H$_2$O) 1:1	pH (KCl) 1:1	pH (NaF) 1:50	O.C.(1) %	K	Ca	Mg	CEC NH4OAc meq/100g	Base Sat. %
Quillayute									
A1p	5.10	4.20	10.90	16.3	0.50	8.20	2.70	65.2	17
A12	5.35	4.45	11.20	13.2	0.50	1.80	0.60	57.1	5
A31	5.30	4.30	11.20	8.0	0.40	1.10	0.25	52.0	3
A32	5.05	4.30	11.40	6.6	0.30	0.70	0.20	41.5	3
B2	5.00	4.55	10.80	2.2	0.15	0.55	0.05	32.7	2
Hembre 1									
A1	4.10	3.90	10.20	11.7	0.15	1.00	1.30	51.0 (2)	5
B21	4.25	4.00	10.80	9.4	0.15	1.00	1.25	50.4	5
B22	4.95	4.10	11.00	3.2	0.05	0.35	0.55	37.8	3
B32	5.00	4.10	10.70	1.6	0.05	0.35	0.75	37.8	3
C	5.20	4.00	9.90	0.6	0.15	1.35	2.10	40.0	9
Hembre 2									
A1	4.40	4.20	11.25	15.1	0.85	2.70	2.10	63.1 (2)	7
B21	4.45	4.30	11.50	12.1	0.45	0.70	0.55	57.2	3
B22	4.50	4.30	11.55	11.6	0.35	0.40	0.35	58.8	2
B32	4.80	4.50	11.50	7.5	0.15	0.35	0.15	44.4	1
C	5.10	4.60	11.30	4.9	0.15	0.25	0.05	44.3	1
Knappa									
A11	5.00	4.10	10.55	11.7	0.25	1.40	1.20	58.0	5
A12	5.10	4.20	11.00	6.4	0.65	1.90	1.60	51.9	8
B21	5.10	4.15	10.80	0.9	0.15	0.90	1.60	48.5	6
B22	5.15	4.00	10.10	0.4	0.15	1.40	4.70	54.4	12
Nehalem									
Ap	5.40	4.20	8.10	4.2	0.20	23.30	6.40	44.3	63
B21	5.70	4.30	9.10	2.5	0.15	25.20	6.40	36.1	89
B22	5.65	4.40	9.25	2.0	0.20	30.20	7.60	49.3	77
B32	5.90	4.50	9.10	1.5	0.20	31.50	7.60	50.7	78
Woodburn									
Ap	5.40	4.10	8.80	1.6	0.60	5.70	0.30	15.3	43
A12	5.60	4.20	7.80	0.8	0.45	6.50	1.60	17.1	50
B1	5.60	4.30	7.60	0.4	0.40	11.20	3.50	21.9	69
B2t	5.70	4.30	7.50	0.2	0.40	15.20	5.20	28.2	74
B3t	6.00	4.40	7.50	0.1	0.40	17.00	6.00	26.1	90
Jory									
A1	5.70	4.50	7.40	5.3	5.30	11.95	7.00	45.6	51
A3	5.60	4.30	7.40	4.5	2.30	12.20	6.30	55.1	39
B1	5.40	4.20	7.50	3.4	0.65	11.70	6.60	43.4	44
B21	5.10	4.20	7.40	2.3	0.35	9.80	7.20	39.1	44
B22	5.00	4.10	7.70	1.3	0.20	8.40	6.60	36.4	42
B3	4.80	4.00	7.60	0.7	0.20	8.20	3.70	44.7	27

(1) organic carbon
(2) values for CEC of the two Hembre profiles taken from Meurisse (1972).

Exchange Acidity and Exchangeable Aluminum

Consideration will first be given to the nature of results obtained by successive extractions with neutral KCl using the Knappa profile as an example (Table 2, Figure 1). The sum of Al from the first two extractions, or from a total of 100 ml extractant corresponds to the Coleman value for exchangeable Al (Lin and Coleman, 1960). The values for exchangeable Al obtained by extrapolation to 480 ml extractant by means of a tangent to the extraction curves are the Rich values (Dewan and Rich, 1970). The same tangent drawn to the ordinate furnishes the extrapolated value according to Skeen and Sumner (1965).

In both extrapolations a small error is involved. The Rich value is slightly too high because the extraction curves do not become strictly linear (Table 2). Linearity presumably can be achieved only by using an acidified extractant (Skeen and Sumner, 1965), or possibly with an increased number of extractions. For this same reason the Skeen value is also an approximation. At this point, it should also be stressed that the Coleman and Rich values are obtained by the same methods originally proposed by these authors. However, with regard to the Skeen values, solely the approach of the authors (Skeen and Sumner, 1965) was used and adapted to neutral KCl; their original method was designed for acidified 0.2 $\underline{N}$ NH_4Cl as an extractant, and the samples were shaken and centrifuged rather than leached.

Table 2. Exchange acidity (EA) and exchangeable Al (Ex. Al) of
Knappa extracted with neutral KCl.

| Horizon	Extractable No.	EA	Σ EA	Ex. Al	Σ Ex. Al
				meq/100g	
A11	1	8.02		7.58	
	2	2.62	10.64	2.55	10.13
	3	1.91		1.42	
	4	1.72		1.18	
	5	0.91		0.77	
	6	0.76		0.69	
	7	0.67		0.61	
	8	0.62	17.23	0.67	15.47
A12	1	6.55		5.89	
	2	1.95	8.50	1.96	7.85
	3	1.36		1.31	
	4	0.96		0.89	
	5	0.75		0.69	
	6	0.60		0.55	
	7	0.51		0.40	
	8	0.46	13.14	0.39	12.08
B21	1	12.96		11.78	
	2	3.05	16.01	2.96	14.74
	3	1.91		1.36	
	4	1.11		0.93	
	5	0.88		0.73	
	6	0.68		0.52	
	7	0.63		0.49	
	8	0.56	21.78	0.43	19.20
B22	1	23.25		22.12	
	2	3.24	26.49	2.96	25.08
	3	1.91		1.36	
	4	1.08		0.82	
	5	0.87		0.82	
	6	0.64		0.56	
	7	0.57		0.55	
	8	0.46	32.06	0.34	29.69
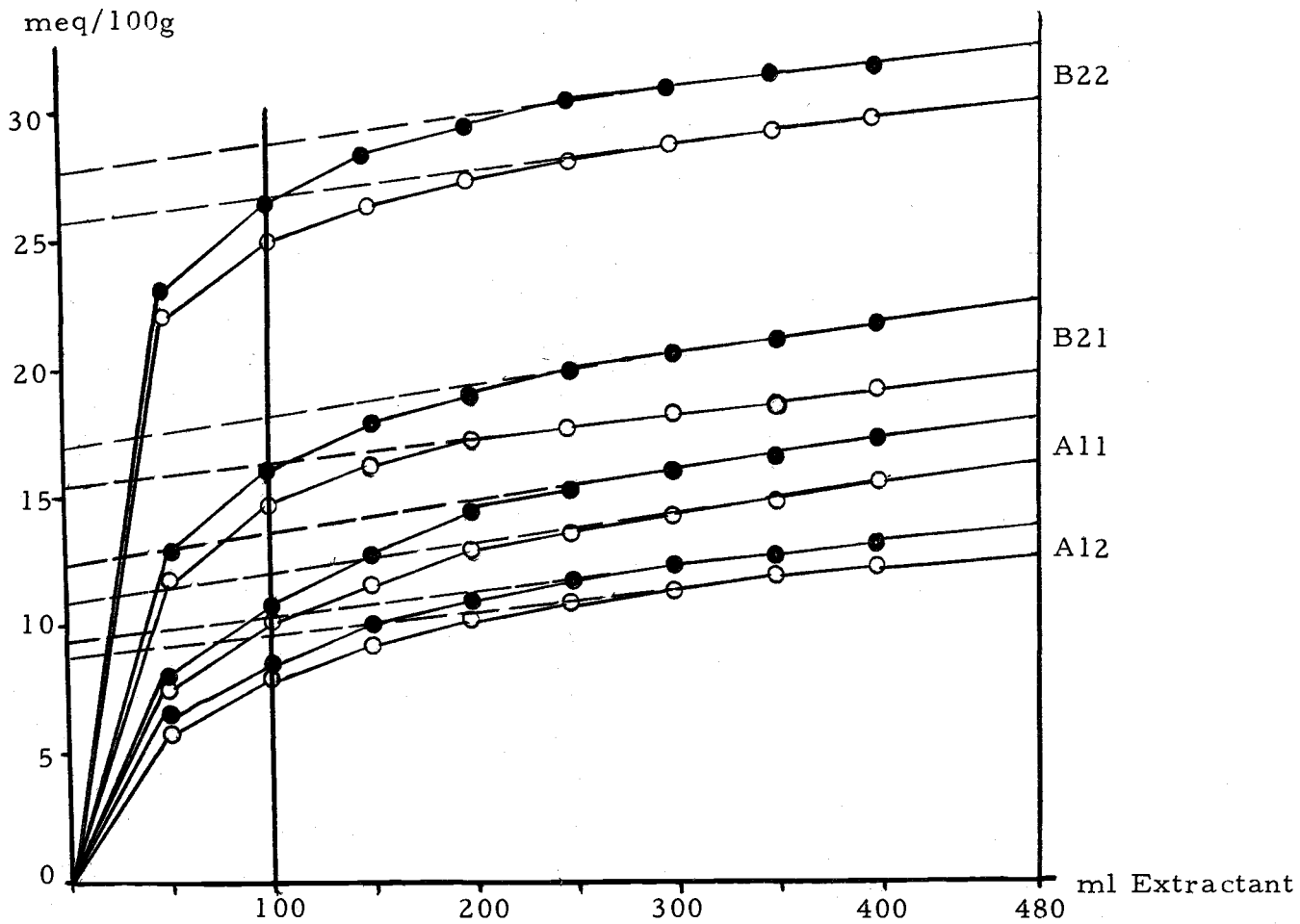
Figure 1. Exchange acidity (●——●) and exchangeable Al (o——o) of Knappa.

The acidity extracted in excess of exchangeable Al is consistently low, mostly from 1 to 2 meq/100 g according to Rich values, and mostly below 0.5 meq/100 g according to Coleman values. According to Dewan and Rich (1970) and Kaddah and Coleman (1967), this small amount of acidity results from hydrolysis of Al held in the interlayer space of lattice clays. The values for exchange acidity and exchangeable Al obtained by the method of Coleman and Skeen, respectively, generally agree within 1 meq (Table 3). The correlation coefficient is very high ($r_{xy} = 0.998$). Hence, it would seem unnecessary to employ the method of successive extractions and extrapolation to determine exchangeable Al unless very accurate data are desired.

The Rich values for exchangeable Al exceed the Coleman values in varying amounts. The ratio of Coleman over Rich values varies depending on the amount of exchangeable Al present, and on the steepness of the final slope of the extraction curves (Table 3). For each profile this ratio increases with increasing content of exchangeable Al. This merely reflects the fact that the Al extracted after the first two extractions becomes less significant if the soil is high in exchangeable Al. Despite their low content of Al, Jory, Woodburn and Nehalem have comparatively higher Coleman/Rich ratios. But the steepness of their final slope is also much lower than in the other coastal soils.

In coastal soils the final slopes of the extraction curves of exchangeable Al correlate significantly with the total organic carbon

Table 3. Exchange acidity and exchangeable Al according to the methods of Coleman (Col), Skeen, and Rich.

| Soil and Horizon	Exchange Acidity			Exchangeable Al			Slope Ex. Al	Col/ Rich
	Col	Skeen	Rich	Col	Skeen	Rich		
	meq/100g			meq/100g			meq/100g	%
Quillayute								
A1p	1.75	1.50	5.00	1.53	1.10	3.95	0.59	39
A12	6.99	7.40	12.55	6.90	7.20	11.90	0.98	58
A31	5.55	6.30	11.45	5.59	5.95	9.70	0.78	58
A32	4.83	5.10	9.00	4.48	4.90	8.20	0.69	55
B2	1.52	1.65	4.25	1.28	1.55	3.20	0.34	40
Hembre 1								
A1	15.60	17.00	23.10	14.75	16.30	21.10	1.00	70
B21	11.03	11.60	17.50	10.47	11.40	15.65	0.89	67
B22	8.52	8.90	13.30	7.09	7.60	11.50	0.81	62
B3	10.96	11.30	17.00	9.32	10.50	14.40	0.81	65
C	21.25	22.40	25.90	20.32	20.90	24.60	0.77	82
Hembre 2								
A1	5.90	6.70	12.70	5.79	6.60	11.50	1.02	50
B21	4.69	5.10	10.90	4.66	4.60	10.10	1.05	46
B22	4.99	4.90	11.70	4.82	4.80	10.50	1.19	46
B3	2.45	2.10	7.10	2.29	1.90	6.05	0.87	38
C	1.59	1.20	5.40	1.40	1.20	4.50	0.69	31
Knappa								
A11	10.64	12.20	18.00	10.13	10.80	16.20	1.27	63
A12	8.50	9.20	14.00	7.85	8.80	12.80	1.03	61
B21	16.10	16.80	22.70	14.74	15.40	19.90	1.09	74
B22	26.49	27.70	32.80	25.07	25.80	30.50	1.13	80
Nehalem								
Ap	2.58	2.62	5.10	1.92	2.31	3.60	0.28	53
B21	1.51	1.63	3.30	1.13	1.21	2.45	0.26	46
B22	0.87	0.75	2.15	0.58	0.76	1.25	0.10	46
B32	0.51	0.58	1.70	0.17	0.15	0.60	0.05	30
Woodburn								
Ap	1.55	1.85	2.90	1.14	1.18	1.80	0.13	63
A12	0.86	0.94	1.96	0.63	0.72	1.10	0.08	57
B1	1.04	1.10	2.00	0.70	0.82	1.04	0.05	67
B2t	0.77	1.02	1.58	0.46	0.55	0.74	0.04	62
B3t	0.47	0.55	1.00	0.18	0.22	0.35	0.02	51
Jory								
A1	0.39	0.47	1.07	0.10	0.10	0.20	0.02	50
A3	0.64	0.70	1.80	0.29	0.27	0.80	0.11	36
B1	0.80	0.85	2.17	0.42	0.45	1.04	0.12	40
B21	1.04	1.24	2.56	0.72	0.88	1.61	0.06	45
B22	2.00	2.28	3.64	1.39	1.35	2.42	0.22	58
B3	2.54	2.84	4.34	1.96	2.10	3.17	0.22	62
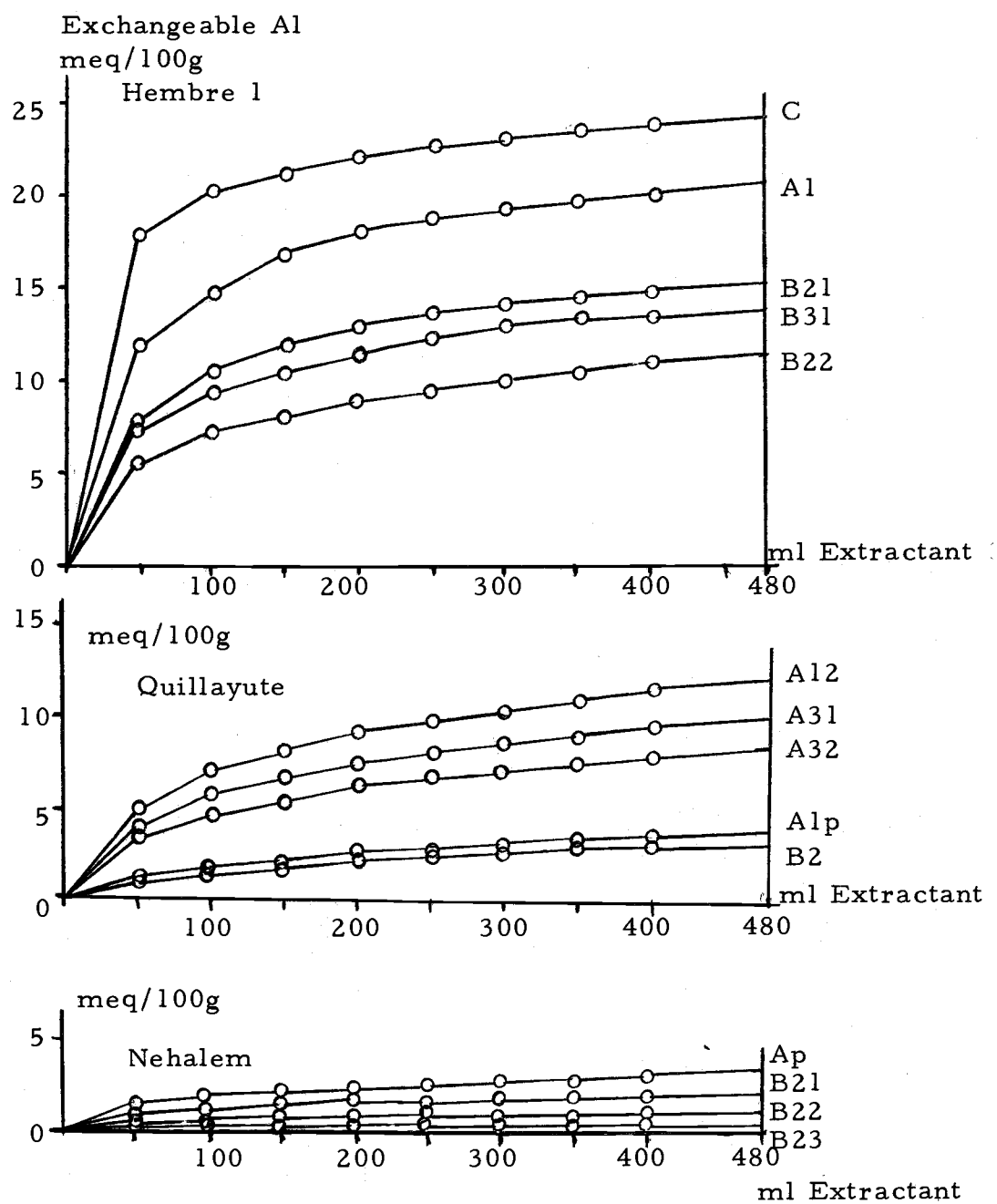
Figure 2. Exchangeable Al of selected soil profiles.

$(r_{xy} = 0.4398**)$, and with the Coleman values for exchangeable Al

$(r_{xy} = 0.4581**)$. Organic matter may possibly correlate with the

slopes because of its attachment to mineral surfaces through cation

bridges with Al. The slopes in Jory, Woodburn, and Nehalem are

much lower than in coastal soils. Hence, the other coastal soils, in

addition to being higher in exchangeable Al, also have a stronger

supplying power for exchangeable Al.

Attempting to explain the various levels of exchangeable Al in

the different profiles would be largely speculative. Birrel's (1962)

hypothesis for volcanic ash soils, which states that the acidity reaches

a maximum with a moderate degree of weathering, does not necessarily

apply to the soils used in this study. In addition, knowledge about the

parent materials and the relative ages of these soils is insufficient to

allow inferences concerning the levels of exchangeable Al.

Quillayute and the two Hembre profiles are currently classified

as Dystrandepts (Franklin, 1970; Meurisse, 1972). Compared to the

very limited data published on Dystrandepts and ando-like soils (Igue

and Fuentes, 1972; Dewan and Rich, 1970), the soils used in this study

are extremely high in exchangeable Al. This is in contradiction to

the concept of Dystrandepts as soils with low contents of exchangeable

Al (Soil Survey Staff, 1970, p. 12-10).

As stated earlier, the values obtained by the methods of Coleman

and Skeen agree quite well, whereas Rich's method furnishes

substantially higher values. Hence, the question arises which one of the methods should be credited with being the closest approximation of reality.

Judging from the form of the extraction curves, particularly in soils high in exchangeable Al (Table 3, Figures 1 and 2), it seems reasonable to believe that two distinctly different forms of Al are extracted; one form, corresponding to the steep initial part of the curve, is readily exchangeable and released against neutral salts ; the flat part of the curve seems to correspond to a slowly released form that is not exchangeable in a strict sense. Hence, Skeen's approach of extrapolation appears to be realistic. The good agreement between the methods of Coleman and Skeen is not completely coincidental since the slope of the curve generally decreases substantially after 100 ml of extractant. This limit was originally chosen because it was felt that Al extracted above this point was negligible (Lin and Coleman, 1960). This, however, is not true for soils high in exchangeable Al (e. g. , Knappa, Table 2), in which appreciable amounts of Al are obtained in the third and fourth extraction.

To further test the various methods a comparison of the exchangeable cations and the cation exchange-capacity by a neutral salt appeared to be useful (Table 4, Figure 3). The exchangeable cations are the sums of the exchangeable bases and either the Coleman or Rich values for exchangeable Al.

Table 4. Exchangeable cations and neutral salt CEC.

| Soil	Horizon	Exchangeable Bases	Exchangeable Cations Coleman	Exchangeable Cations Rich	Neutral salt CEC
		---------------- meq/100g----------------------			
Quillayute	A1p	11.40	12.95	15.35	12.10
	A12	2.90	9.90	14.80	8.20
	A31	1.80	7.35	11.50	5.40
	A32	1.10	5.65	9.30	4.50
	B2	0.75	2.05	3.95	1.10
Hembre 1	A1	2.45	17.20	23.55	15.90
	B21	2.40	12.85	18.00	9.90
	B22	0.95	8.05	12.45	5.80
	B3	1.15	10.50	15.55	17.60
	C	3.60	23.95	28.20	18.90
Hembre 2	A1	4.65	10.45	16.15	10.60
	B21	1.70	6.35	11.80	4.40
	B22	1.10	5.95	11.60	4.20
	B3	0.65	2.95	6.65	2.60
	C	0.45	1.90	4.95	2.10
Knappa	A11	2.85	12.95	19.05	11.20
	A12	4.15	12.00	16.95	7.30
	B21	2.65	17.40	22.55	12.50
	B22	6.25	31.30	36.75	26.00
Nehalem	Ap	27.90	29.90	31.50	29.30
	B21	32.15	33.30	34.65	30.80
	B22	38.00	38.55	39.20	40.50
	B32	39.60	39.75	40.20	41.10
Woodburn	Ap	6.55	7.70	8.35	8.00
	A12	8.55	9.15	9.65	8.80
	B1	15.20	15.80	16.20	14.60
	B2t	20.80	21.30	21.50	20.30
	B3t	23.40	23.60	23.80	22.00
Jory	A1	23.25	23.35	23.45	25.20
	A3	20.80	21.10	21.60	22.10
	B1	18.95	19.35	20.00	21.10
	B21	17.35	18.05	18.95	19.60
	B22	15.20	16.60	17.60	17.50
	B3	12.10	14.70	15.30	16.70
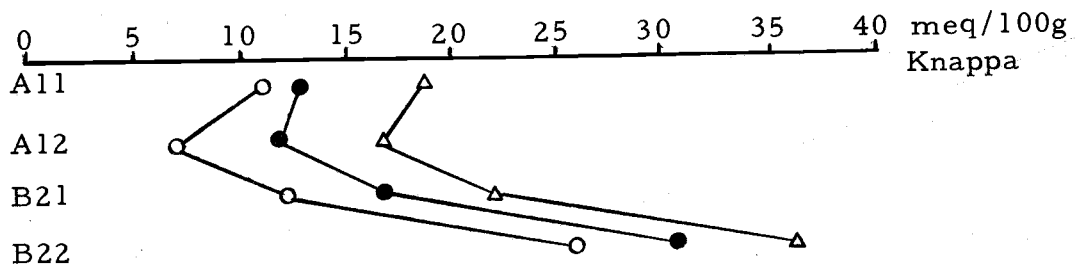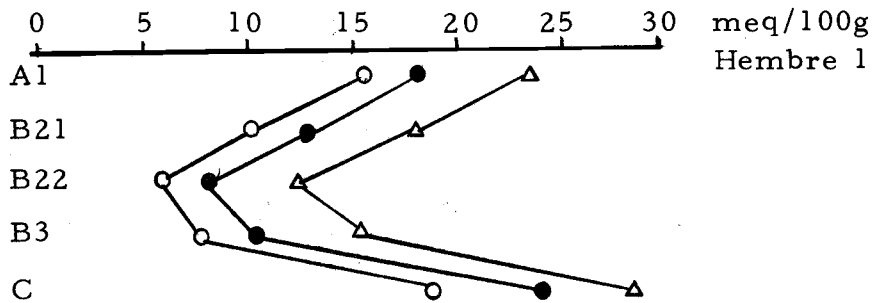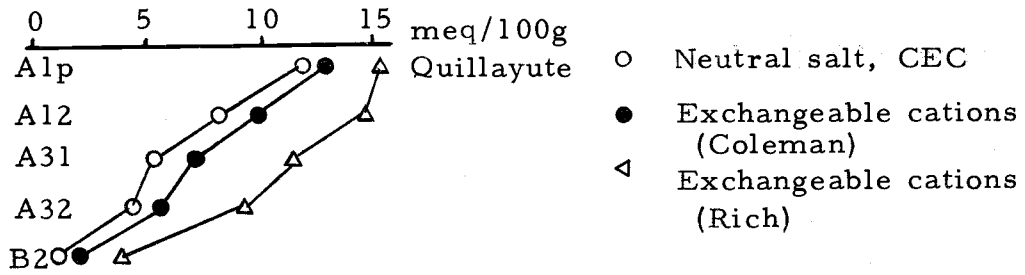
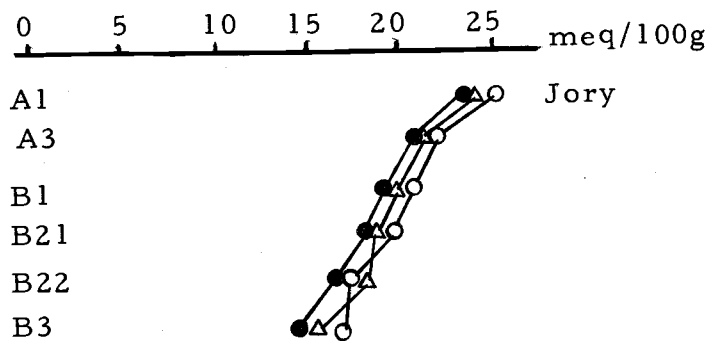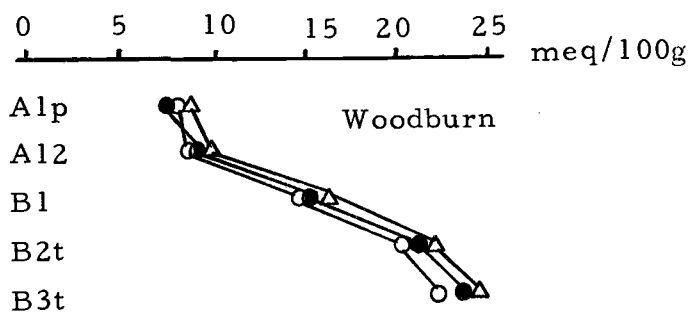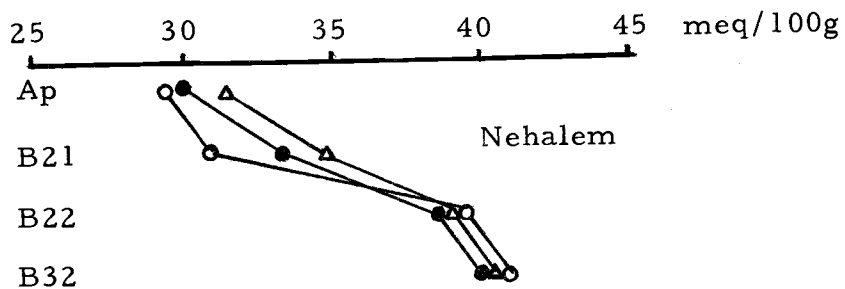Figure 3. Exchangeable cations and neutral salt CEC.

Figure 3.   (Continued)

Good agreement between the Rich and Coleman values for exchangeable cations with the neutral salt CEC can be observed in the Nehalem, Woodburn and Jory soils. In these soils exchangeable Al is not the dominant cation on the exchange complex, and therefore the variation due to the different methods for the determination of exchangeable Al does not significantly influence the results. In addition, the exchangers in these soils appear to be of a nature that does not result in strongly differing values due to salt retention and hydrolysis characteristic for amorphous exchangers.

Significant differences are evident in the results of the four other soils in which Al is the dominant cation on the exchange complex. The neutral salt CEC is generally from 2 to 3 meq lower than the Coleman value for exchangeable cations, and this difference reaches maxima around 5 meq in the Knappa and Hembre 1 soils. It is possible to explain this difference in terms of the methods used for the CEC determination. Conventional methods of CEC determination, such as the one used in this study, have inherent errors due to the washing step with water (Ensminger, 1944; Schofield, 1949; Okazaki et al., 1962; Wada and Harada, 1969; Reeve and Sumner, 1971; Smith et al., 1966). Thorough washing, sufficient to avoid salt retention, apparently removes some of the index cation from exchange sites by hydrolysis and leads to values less than the true CEC. The effect is particularly pronounced in amorphous aluminosilicates, such as

allophane which, in addition, shows as a yet unexplained cation species effect (Wada and Harada, 1969).

The difference between neutral salt CEC and the Rich value for exchangeable cations ranges up to 10 meq/100 g, and it cannot be accounted for by these same mechanisms. Again the conclusion is that the method of Rich for exchangeable cations furnishes values that are not compatible with other standard methods, and that non-exchangeable forms of Al appear to be included.

This latter conclusion, based on the comparison between exchangeable cations and neutral salt CEC, is not strictly valid. Firstly, the definition of CEC is still largely a matter of convention. The three most common definitions of CEC are the quantities of cations absorbed from either natural salt solutions or from salt solutions buffered at pH 7 or 8.2 (Coleman and Thomas, 1967). The neutral salt CEC is presumably the closest reflection of the exchange capacity of a soil in its natural state, since the pH of the system remains practically unaltered, and thus no significant changes in the charge distribution are induced. Secondly, within one definition of CEC, e.g., neutral salt CEC, there is extensive variation in the specific procedure of determination. It could possibly be argued that good agreement could be achieved between the Rich values for exchangeable cations and neutral salt CEC, if in the determination of the latter, a method was used that involved an equivalent volume of both saturating

and exchanging solution as in the method of Rich to determine exchange-able Al. Hence, the conclusion that Rich's method furnishes too high values can only be made relative to other standard methods. But it is felt that this conclusion can be maintained on the basis of the shape of the extraction curves, as mentioned before.

Organically Bound Al and Fe

The proportion of organic matter of the upper horizons contained in the humic acid fraction is generally higher in grassland soils than in forest soils (Mortensen and Himes, 1964). The data in Table 5 indicate that among the coastal soils, only Quillayute has developed under a non-forest vegetation. This is in agreement with the types of original vegetation assumed for these soils (Bowlsby and Swanson, 1964). According to Habeck (1961), the Mid-Willamette Valley, at the time of settlement, was covered with oak openings and prairie, whereas the Douglas-fir forest type dominated both the western and eastern sides of the mid-valley transects. This agrees with the organic matter data for Jory and Woodburn. The decrease of the ratio of humic to fulvic acid with depth presumably reflects the predominant illuviation of the more mobile fulvic fraction (Wright and Schnitzer, 1960). This decrease is virtually absent in Nehalem, possibly a result of the fluventic character of this soil.

Table 5. Organic carbon in humic (H. A.) and fulvic acid (F. A.) extracted with Na-pyrophosphate.

Soil and Horizon	Humic Acid	Fulvic Acid	H. A. /F. A.	Cext/Ctotal (1)
	-------% Organic Carbon ------			%
Quillayute				
A1p	4.95	2.15	2.3	43
A12	4.55	2.05	2.2	50
A31	2.70	1.25	2.1	49
A32	2.20	1.15	1.9	51
B2	0.25	0.65	0.4	41
Hembre 1				
A1	2.10	2.75	0.8	42
B21	1.15	2.10	0.6	35
B22	0.40	0.75	0.5	36
B3	0.20	0.35	0.6	34
C	0.05	0.15	0.3	33
Hembre 2				
A1	2.45	3.10	0.8	37
B21	1.35	3.05	0.4	36
B22	1.40	3.20	0.4	40
B3	0.70	2.10	0.3	38
C	0.20	1.50	0.2	36
Knappa				
A11	1.80	1.70	1.1	30
A12	0.85	1.10	0.8	31
B21	0.15	0.20	0.7	38
B22	0.05	0.25	0.5	38
Nehalem				
Ap	0.60	0.70	0.9	31
B21	0.35	0.40	0.9	30
B22	0.25	0.35	0.7	30
B23	0.20	0.25	0.8	28
Woodburn				
Ap	0.50	0.20	2.5	44
A12	0.25	0.15	1.7	50
B1	0.10	0.10	1.0	50
B2t	0.05	0.05	1.0	50
B3t	0.01	0.02	0.5	30
Jory				
A1	0.85	0.65	1.3	28
A3	0.70	0.60	1.2	29
B1	0.65	0.45	1.4	32
B21	0.40	0.35	1.1	33
B22	0.10	0.25	0.4	27
B3	0.05	0.15	0.3	27

(1) Organic carbon extracted by pyrophosphate over total organic carbon.

The ratio of carbon extracted by pyrophosphate to total carbon (Cext/C total, Table 5) ranges from about 30% to 50%. This roughly corresponds to published values (McKeague, 1968). Neither the percentage of extractable carbon, nor the ratio of humic to fulvic acid, clearly differentiates between A and B horizons.

The level of organic matter in a soil represents an equilibrium between additions and losses. Little is known about the biology of organic matter decomposition, and its relation to different chemical and mineralogical conditions in soils. The single most important factor in organic matter stabilization is still the adsorption of organic matter on mineral surfaces (Ensminger and Gieseking, 1942; Mortland and Gieseking, 1952). Greenland and Ford (1964) have reported that 98% of the total organic carbon in a Lateritic Red Earth was associated with the clay fraction. Other factors include inaccessibility of organic matter to microbes, and toxic effects of elements, such as Al, on microbial activity.

The pyrophosphate extraction was carried out to test whether its results would help to explain the large organic matter accumulations in coastal soils. The pyrophosphate data will be discussed mainly in terms of the concepts of Mortland (1970) and Greenland (1971) on the types of bonding between organic matter and inorganic surfaces which are perhaps the most comprehensive ones forwarded thus far in this area. In brief summary, the essential elements of these concepts are

(1) an increased emphasis of the chemical nature of the inorganic surfaces involved in organic matter adsorption, and (2) a qualitative distinction of different types of bonding. These types of bonding include anion exchange, coordination bonds, polyvalent cation bridges, ligand exchange, hydrogen bonding, and van der Waals forces.

The contents of Al and Fe in the fulvic fraction of the Quillayute and Knappa samples were found to be much higher than in the humic fraction (Table 6). This does probably not represent natural conditions. Riffaldi and Schnitzer (1972) have shown the contents and kinds of functional groups in humic and fulvic acid to be somewhat similar. Hence, similar contents of Al and Fe would be expected in the two fractions. It is therefore concluded that pyrophosphate complexes Al and Fe previously associated with organic matter and these soluble complexes appear in the fulvic fraction after the precipitation of the humic fraction. The residual Al and Fe in the humic fraction seems to correspond to a fraction strongly held by the organic molecules, and may be related to the resistance of organic matter against decomposition.

Table 6. Al and Fe in humic (H. A.) and fulvic acid (F. A.)

Soil and Horizon	H.A. -Al	H.A. -Fe	F.A. -Al	F.A. -Fe
	------------------ mmol/100g soil ----------------------------			
Quillayute				
A1p	4.90	0.40	53.75	13.10
A12	6.35	0.20	59.60	14.60
A31	5.90	0.10	51.80	12.20
A32	4.70	0.05	48.90	12.25
B2	1.70	0.05	21.80	5.20
Knappa				
A11	1.10	0.20	15.90	3.95
A12	0.90	0.10	15.50	4.10
B21	0.30	0.05	9.60	0.60
B22	0.20	0.05	9.10	0.50

Some inference regarding the kinds of bonds broken by pyro-phosphate can be made using the models of Mortland (1970) and Green-land (1971). It is assumed that Al and Fe are organically bound given the fairly good correlations between the organic carbon and Al and Fe extracted by pyrophosphate (Table 8). The types of bonds that are probably affected by pyrophosphate at pH 10 include anion exchange, polyvalent cation bridges, coordination bonds, and possibly ligand exchange, but it is uncertain whether Al and Fe are involved in ligand exchange would be extracted. The only type of bond that directly in-volves polyvalent cations is the cation bridge. Hence, it is possible that Al and Fe extracted by pyrophosphate are a rough estimate of the Al and Fe involved in cation bridges. The ease with which pyrophos-phate appears to complex organically bound Al and Fe would support this conclusion. The question remains whether a cation in a cation bridge of a molecule that is not extracted would be extracted as well.

Since the separation of Al and Fe into a humic and fulvic fraction does not provide any further information, the data for all the profiles are given as total sums (Table 7). The contents of Al and Fe in the different profiles vary considerably. In most cases Al is four to five times higher than Fe. Hembre 1 and, to a lesser extent, Jory, are exceptional in that the amount of Fe nearly equals the amount of Al. Franklin (1970) using H_2O_2 and NaOAc to extract organically bound Fe and Al found similar values for Al in similar soils, but his Fe

Table 7: Total Al, Fe, and organic carbon extracted by Na-pyrophosphate.

Soil and Horizon	Al	Fe	Al+Fe	Organic Carbon %	Al/ O.C.(1)	Fe/ O.C.	Al+Fe O.C.(1)
	------- mmol/100g ---------				-------- mmol/100g ------------		
Quillayute							
A1p	58.6	13.5	72.1	7.10	8.2	1.9	10.1
A12	66.0	14.8	80.0	6.60	9.6	2.2	11.8
A31	57.7	12.3	70.0	3.95	14.1	3.1	17.2
A32	53.6	12.3	65.9	3.35	15.6	3.7	13.3
B2	23.5	5.2	28.7	0.90	25.6	8.0	33.6
Hembre 1							
A1	48.0	43.4	91.4	4.85	8.9	8.9	17.6
B21	48.4	47.2	95.6	3.25	13.7	14.5	28.0
B22	36.5	31.3	68.4	1.15	30.0	27.2	57.2
B3	26.4	17.1	43.5	0.55	42.2	31.3	73.5
C	17.6	5.3	22.9	0.20	53.8	26.6	80.4
Hembre 2							
A1	22.4	3.9	26.3	5.55	3.7	0.7	4.4
B21	25.3	5.4	30.7	4.40	5.5	1.2	6.7
B22	26.0	5.4	31.4	4.60	5.3	1.2	6.5
B3	23.0	4.2	27.2	2.80	7.9	1.5	9.4
C	16.2	2.7	18.9	1.70	9.2	1.6	10.8
Knappa							
A11	17.0	4.1	21.1	3.50	3.9	1.2	5.1
A12	16.4	4.2	10.6	1.95	7.1	1.2	9.3
B21	9.9	0.6	10.5	0.35	14.0	1.9	16.9
B22	9.3	0.5	9.8	0.30	6.7	3.7	10.4
Nehalem							
Ap	6.5	1.5	8.0	1.30	4.7	1.1	5.8
B21	4.9	1.6	6.5	0.75	6.1	2.1	8.2
B22	4.2	1.0	5.2	0.60	6.7	1.7	8.4
B23	3.4	0.9	3.3	0.45	7.6	2.1	9.7
Woodburn							
Ap	7.9	1.4	9.3	0.70	10.7	2.1	12.8
A12	6.4	1.5	7.9	0.40	15.5	3.7	19.2
B1	3.6	0.7	4.3	0.20	17.0	3.5	20.5
B2t	3.0	0.6	3.6	0.10	28.0	6.0	34.0
B3t	2.7	0.5	3.2	0.05	86.5	.	104.9
Jory							
A1	6.2	4.4	10.6	1.50	4.1	3.0	7.1
A3	7.2	4.1	11.3	1.30	5.4	3.2	8.6
B1	5.7	3.7	9.4	1.10	5.0	3.4	8.4
B21	4.5	3.3	7.8	0.75	5.6	4.4	10.0
B22	3.8	2.5	6.3	0.35	9.7	7.3	17.0
B3	2.7	1.7	4.4	0.20	10.5	8.8	19.3

(1) Al and/or Fe/organic carbon extracted by pyrophosphate; in these ratios exchangeable Al determined by the method of Lin and Coleman (Table 3) was subtracted from the pyrophosphate extractable Al.

values, e. g. , in the Quillayute soil, are about three times lower than

the values obtained in this study.   This difference is most likely a

result of the use of different extractants.

Table 8.   Linear correlation coefficients between Al, Fe and organic carbon (O. C.) extracted by Na-pyrophosphate.

Soil	Al - O. C. (1)	Fe - O. C.	(Al + Fe) - O. C. (1)
Quillayute	0. 8762**	0. 8856**	0. 8719**
Hembre 1	0. 8532**	0. 8687**	0. 8627**
Hembre 2	0. 5886 n. s.	0. 5954 n. s.	0. 6117 n. s.
Knappa	0. 8922**	0. 9099**	0. 9000**
Nehalem	0. 9950***	0. 7499 n. s.	0. 9702***
Woodburn	0. 9753***	0. 9641***	0. 9706***
Jory	0. 9566***	0. 9818***	0. 9737***

(1) Al values reduced by the amounts of exchangeable Al (Coleman values, Table 3).
**   Significant at the 5% level.
*** Significant at the 1% level.
n. s. Non-significant.

If it is assumed that the source of the Al and Fe extracted is

predominantly the polyvalent cation bridge, the fact that more Al than

Fe was extracted does not necessarily contradict the finding (Schnitzer

and Hansen, 1970; Scharpenseel, 1966) that Fe forms more stable

complexes with organic matter, and that Fe is more efficient as a

bridging cation.   It most likely reflects the higher availability of Al

in soils to form complexes and bridges.   It is also possible that Fe

bridges are less readily extracted by pyrophosphate than Al bridges.

The ratios of pyrophosphate extractable Al or Fe to the extracted organic carbon invariably increase more or less strongly with depth. A similar trend is shown in the data of Flach (1970) for a Dystrandept and a Haplumbrept. There are several possible reasons for this. Firstly, it is possible that the metal content of the organic matter increases with depth in the soil in its natural state. Fulvic acid is evidently transferred to lower horizons (Table 5). Schnitzer and Skinner (1963) have shown that the solubility in water of organic matter complexes with Al and Fe decreases as the metal content increases. In another report, Wright and Schnitzer (1963) suggested that in podzols, fulvic acid on its way down the profile first exists as a water soluble chelate with Al and Fe, and that precipitation of this complex occurs lower in the profile due to further reaction with the same metals. According to the models of Greenland (1971) and Mortland (1970), the stabilization of fulvic acid in lower horizons should probably be explained in terms of the availability of inorganic mineral surfaces rather than in terms of increasing metal content of the organic complexes. As the organic matter decreases with depth there will be a concurrent increase in inorganic surfaces available for organic matter adsorption. However, it would not explain the increase in metal content with depth unless it is assumed that polyvalent cation bridges constitute the predominant form of bonding in

lower horizons. This cannot be answered on the basis of the data presented here. Secondly, it could be argued that pyrophosphate extracts increasing amounts of inorganic Al and Fe as the portion of organic matter relative to the inorganic fraction decreases. The ability of pyrophosphate to dissolve oxides of Al and Fe has been pointed out by some authors (Titova, 1962; Duchaufour, 1964; Grimme and Wiechmann, 1969), but denied by others (McKeague, 1967). Thirdly, and this concerns the lowest horizons of some soils, such as Hembre 1 and Woodburn, which are very low in organic matter, the limit of accuracy of the method to determine organic matter was reached, and the values for humic and fulvic acid are probably too low. This could be the reason for the very high ratios of metal to organic matter found in these horizons.

Considering the ratio Fe/O.C., Hembre 1 and, to a lesser extent, Jory are higher than the other soils. Whereas the values for Jory can possibly be explained in terms of its high content of Fe (Table 9), no plausible explanation could be found for Hembre 1. To answer this question a much better identification of different forms of Fe oxides and their behavior relative to various extractants would be required; however, the methods to achieve this are presently not available.

To discuss the large organic matter accumulations in coastal soils, the pyrophosphate data of the top horizons only will be

considered. The Al/O. C. and Fe/O. C. ratios in some soils (Quilla-
yute, Woodburn) are roughly two to three times as high as in other
soils (Hembre 2, Nehalem). The meaning of these variations is not
clear. It is possible that a better understanding could have been
achieved had other bridging cations such as Ca and NH_4 also been
determined. In addition, the possibility of differential solution of
inorganic oxides of Al and Fe could also be a reason for these vari-
ations.

In soils that are high in organic matter the absolute amounts of
Fe and Al extracted by pyrophosphate are higher than in soils low in
organic matter. This would also be true for the absolute amounts of
cation bridges, if the amounts of pyrophosphate extractable Al and Fe
are indeed approximations of the amounts of cation bridges in the
soils. The Al/O. C. and Fe/O. C. ratios show no relationship to the
total organic carbon of these soils. The relative similarity of these
ratios suggests that the portions of organic matter bonded to inorganic
surfaces by cation bridges have similar contents of polyvalent cations.
The explanation for the different levels of pyrophosphate extractable
Al and Fe, and for the different levels of organic matter must there-
fore be sought in the kinds of inorganic surfaces available for organic
matter adsorption.

The extent of adsorption of organic matter on inorganic surfaces
and the kinds of bonds between them appear to be a function of the

available surface area, and of the chemical nature of these surfaces.
It is well known that amorphous aluminosilicates (e. g. , allophane)
have a greater ability to adsorb organic matter than other clay miner-
als (Inoue and Wada, 1968). Many coastal soils, including Quillayute
and Hembre, have been shown to contain considerable amounts of
amorphous aluminosilicates (Franklin, 1970; Meurisse, 1972). If
Mortland's (1970) and Greenland's (1971) models of organic matter
adsorption are applied to the different minerals occurring in soils,
then allophanic materials appear to be the most efficient adsorbers
of organic matter. Allophane combines a high specific surface area
which is presumably largely aluminous with a net negative charge.
Hence, any of the proposed adsorption mechanisms, except anion
exchange, can occur on allophane. The negative charges would pre-
sumably also increase the amount of cation bridges. Other amorphous
oxides of Al have positive charges under acid conditions which would
restrict cation bridges. In phyllosilicates, on the other hand, ligand
exchange is not likely to occur. Furthermore, amorphous oxides and
phyllosilicates have lower specific surface areas.

Some remarks should be made regarding the usefulness of pyro-
phosphate as an extractant. Pyrophosphate is useful insofar as it
appears to approximate the amount of cation bridging in soils. How-
ever, since pyrophosphate extractable carbon correlates significantly
with the total organic carbon (r_{xy} = 0. 9748***) and, on the other hand,

pyrophosphate extractable carbon correlates fairly well with pyro-
phosphate extractable Fe and Al (Table 8), it could be argued that the
total contents of organic carbon in the soils used in this study provide
in fact the same information as the pyrophosphate data. This is not
necessarily true for all types of soils. McKeague (1968) has shown
that pyrophosphate extracts as much as 95% of the total organic carbon
in spodic horizons.

Pedogenetic Oxides

Iron and Al oxides form different types of surfaces which pre-
sumably behave differently with respect to soil properties such as
exchange capacity and organic matter adsorption. Furthermore, the
mere knowledge of absolute quantities of particular types of oxides
formed in a soil under particular conditions would be highly useful for
purposes of soil genesis and classification.

Acid ammonium oxalate has been proposed as an extractant for
amorphous oxides of Fe (Schwertmann, 1959; McKeague and Day, 1966;
Bascomb, 1968; Blume and Schwertmann, 1969). Dithionite, on the
other hand, extracts both amorphous and crystalline forms of Fe
(Mehra and Jackson, 1960; McKeague and Day, 1966; Bascomb, 1968;
Blume and Schwertmann, 1969). Whereas the presumed specificity
of dithionite remained essentially undisputed, except for phyllosilicates
containing Fe (Dudas and Harward, 1971), acid oxalate has been

severely criticized in a recent paper by Pawluk (1970) who considers

its use for specific criteria in soil classification as premature.

Acid oxalate extracts somewhat higher amounts of Al than

dithionite from all soils except Jory (Table 9). This agrees with the

results of McKeague and Day (1966) and Dudas and Harward (1971).

The ratio of oxalate extractable Fe over dithionite extractable Fe

(Fe_{ox}/Fe_{dith}) which has been called the 'active Fe ratio' by Schwert-

mann (1964) does not vary greatly within individual profiles. Larger

variations are apparently only found in soils having horizons with

illuvial accumulations of secondary sesquioxides, and oxalate appears

to be useful to chemically identify these horizons (McKeague and

Day, 1966; Blume and Schwertmann, 1969). The Fe_{ox}/Fe_{dith} ratio

seemingly differentiates between the coastal soils and the Woodburn

and Jory soils. The finding that the ratio in coastal soils is higher

may reflect the inhibition of the crystallization of Fe oxides by organic

compounds reported by Schwertmann et al. (1968). However, Jory

contains appreciable amounts of organic matter together with a very

low ratio throughout the profile indicating that inhibition of crystalli-

zation by organic compounds is probably only one of the factors

involved.

Given the uncertain specificity of the oxalate extraction, and the

absence of any particularly high correlations of either extraction with

other data reported in this study, no further discussion of the oxalate

and dithionite data will be made here.

Table 9. Ammonium oxalate and Na-dithionite-citrate extractable Al and Fe.

Soil and Horizon	Al_{ox}	Fe_{ox}	Al_{dith}	Fe_{dith}	Fe_{ox}/Fe_{dith}
			%		
Quillayute					
A1p	2.38	1.80	2.12	3.30	0.55
A12	2.56	1.75	2.27	3.52	0.50
A31	2.70	1.92	2.22	3.42	0.56
A32	2.76	1.89	2.24	3.42	0.54
B2	2.56	1.60	1.74	3.20	0.50
Hembre 1					
A1	2.30	1.50	1.98	2.70	0.56
B21	2.35	1.55	2.03	2.83	0.55
B22	2.52	1.52	1.79	2.77	0.55
B32	2.32	1.25	1.52	2.61	0.48
C	1.72	0.84	1.14	2.10	0.40
Hembre 2					
A1	3.98	1.39	2.66	3.12	0.45
B21	4.04	1.78	2.93	3.38	0.51
B22	3.99	1.73	3.01	3.67	0.48
B32	4.46	1.45	3.93	3.53	0.41
C	4.68	1.21	2.36	3.05	0.40
Knappa					
A11	2.49	1.48	2.29	2.74	0.54
A12	2.72	1.63	2.19	2.84	0.57
B21	3.36	1.37	1.66	2.37	0.58
B22	2.14	1.35	1.34	2.42	0.56
Nehalem					
Ap	1.01	0.87	0.58	2.24	0.48
B21	0.97	0.79	0.56	2.12	0.47
B22	0.95	0.75	0.48	2.28	0.42
B23	1.00	0.80	0.28	2.32	0.40
Woodburn					
Ap	0.32	0.46	0.28	1.51	0.30
A12	0.25	0.45	0.24	1.46	0.31
B1	0.25	0.46	0.22	1.62	0.28
B2t	0.18	0.37	0.18	1.44	0.26
B3t	0.14	0.32	0.14	1.30	0.25
Jory					
A1	0.80	1.29	0.94	6.29	0.21
A3	0.81	1.26	0.95	6.52	0.19
B1	0.72	1.26	1.05	6.73	0.19
B21	0.71	1.32	1.18	6.90	0.20
B22	0.67	1.43	1.14	7.16	0.20
B3	0.81	1.26	1.28	7.10	0.18

Taxonomy

The official classification of the Quillayute series as a Typic

Dystrandept (Soil Survey Staff, 1972) was verified by Franklin (1970)

(Table 11). The Hembre series is officially classified as a Typic

Haplumbrept, but Meurisse (1972) has shown both profiles used in

this study to be members of the Typic Dystrandept subgroup.

As shown in Table 10, the Knappa profile meets all the require-

ments associated with an exchange complex dominated by amorphous

materials (Soil Survey Staff, 1970), except DTA data which were not

determined. It was classified as a Typic Dystrandept; the official

classification lists the Knappa series as a Pachic Haplumbrept (Soil

Survey Staff, 1972). The only property that does not fit the concept of

this subgroup is the high amount of exchangeable Al found in this pro-

file, but exchangeable Al is not a stated criterion.

Table 10.   Taxonomic data for Knappa.

Horizon	Depth cm	Sand %	Silt (1) %	Clay %	Bulk Density gr/cc
A11	0-20	17.7	67.9	14.6	0.62
A12	20-50	17.1	65.3	17.2	0.62
B21	50-85	26.6	59.9	13.5	0.86
B22	85-105+	30.1	55.5	14.4	

Horizon	pH(NaF)	15 Bar Mois- ture, %	15 Bar Mois- ture/% Clay	CEC/100g Clay (2) meq/100g
A11	10.55	35.1	1.85	396
A12	11.00	29.2	1.68	302
B21	10.80	24.3	1.93	360
B22	10.10	24.5	1.70	378

(1) Silt determined by difference.   (2) CEC by NH_4OAc at pH 7.

The Nehalem profile sampled for this study is a Fluventic Hap-ludoll on the basis of its high base saturation. This corresponds with the data previously published for Nehalem by Bowlsby and Swanson (1964). The Nehalem series is officially classified as a Fluventic Haplumbrept.

Table 11. Official classification of the soil series, and classification of the profiles used in this study.

Soil	Official Series Classification (1)	Classification of Profile
Quillayute	Typic Dystrandept	Typic Dystrandept (Franklin, 1970)
Hembre	Typic Haplumbrept	Typic Dystrandept (Meurisse, 1972)
Knappa	Pachic Haplumbrept	Typic Dystrandept
Nehalem	Fluventic Haplumbrept	Fluventic Hapludoll
Woodburn	Aquultic Haploxeroll	Aquultic Haploxeroll
Jory	Xeric Haplohumult	Xeric Haplohumult

(1) Soil Survey Staff, 1972.

Another question relating to soil taxonomy is the use of pyrophosphate and dithionite in the chemical identification of the spodic horizon. These criteria are: (a) the ratio of Fe plus Al (elemental) extractable by pyrophosphate at pH 10 to percent clay is greater than 0.2, and (b) the sum of pyrophosphate extractable Fe plus Al is more than half of the sum of dithionite-citrate extractable Fe plus Al (Soil Survey Staff, 1970, p. 3-23). None of the soils used in this study

meets the first requirement. There are no particle size distribution data available for the two Hembre soils, but it is assumed that they are sufficiently high in clay to fail the first requirement. Similarly, the second requirement is met in none of the soils except in the first two horizons of Hembre 1. However, spodic horizons have to meet both requirements in addition to two other ones, hence pyrophosphate and dithionite appear to make a clear separation between Spodosols and the Inceptisols used in this study.

Summary and Conclusions

Extractable forms of Al and Fe were studied in five soils from the Coast Range and two soils from the Willamette Valley in Oregon.

Exchangeable Al was determined such that comparisons of three different extraction methods could be made. Values for exchangeable Al obtained by Lin's and Coleman's (1960) method agreed closely with those obtained by Skeen's and Sumner's (1965) method which was adapted for neutral salts. Values measured by the method of Dewan and Rich (1970) exceeded the Coleman values in varying amounts depending on the amount of exchangeable Al present, and on the steepness of the final slope of the extraction curve. The slopes in coastal soils which contain amorphous aluminosilicates were steeper than in other soils indicating that these coastal soils have a stronger supplying power for exchangeable Al.

From the shape of the extraction curves it was concluded that two different forms of Al were extracted by the method of successive neutral salt extractions. One form is readily released against neutral salts and was considered to be truly exchangeable. The other form is slowly released and results probably from mineral solution of amorphous hydrous oxides and possibly also from Al-organic complexes.

The sum of exchangeable cations (Ca, Mg, K) was compared to the neutral salt exchange capacity determined by a standard method. In soils with a high base saturation, good agreement between both Rich and Coleman values for exchangeable cations with the neutral salt CEC was observed. However, significant differences were obtained in soils containing amorphous aluminosilicates and in which Al is the dominant cation on the exchange complex. The neutral salt CEC was generally from 2 to 3 meq lower than the Coleman value for exchangeable cations. These differences were attributed to the underestimation of the CEC due to errors of hydrolysis which are particularly pronounced in allophanic soils. The Rich values for exchangeable cations exceeded the neutral salt CEC by amounts as high as 10 meq/100g. It was concluded that Rich's method to determine exchangeable cations furnishes values that are not compatible with other standard methods, and that non-exchangeable of Al forms appear to be included. However, since the definition of CEC is still a matter of convention, the above conclusion is valid only in terms of presently

accepted methods to determine CEC.

Organic carbon was extracted with pyrophosphate. Humic and fulvic acid were separated, and their content of Al and Fe determined. Humic to fulvic acid ratios were higher in grassland soils than in soils originally under forest vegetation. The amounts of Al and Fe extracted correlate fairly well with the organic carbon extracted by pyrophosphate, hence, pyrophosphate extractable Al and Fe appear to be associated with the organic matter of the soils. The contents of Al and Fe were much higher in the fulvic fraction. It was concluded that pyrophosphate complexes polyvalent cations previously associated with organic matter, and that these complexes appear in the fulvic fraction after the precipitation of the humic fraction. Since polyvalent cation bridges are the only known organo-mineral bonds that consist of ionic Al and Fe, it was concluded that pyrophosphate extractable Al and Fe represent a rough estimate of the Al and Fe involved in cation bridges.

The ratio of Al or Fe to organic carbon, all extracted by pyrophosphate, increased with depth. This could be due to an increase in the metal content of the organic matter, since organic compounds of lower molecular weight (fulvic acid) are evidently transferred to lower horizons, and may thereby increase their metal content. But it is also possible that pyrophosphate extracts increasing amounts of inorganic amorphous Al and Fe as the portion of organic matter

relative to the inorganic fraction decreases. The metal to organic carbon ratios in the top horizons range from 4 to 10 mmol Al/g O. C., and from 0.7 to 3 mmol Fe/g O. C. (except in Hembre 1 in which 8.9 mmol Fe/g O. C. was measured). In soils with a high organic matter content the absolute amounts of Fe and Al extracted by pyrophosphate are higher than in soils with a low organic matter content.

The Al/O. C. and Fe/O. C. ratios show no relationship to the total organic carbon of these soils. The relative similarity of these ratios suggests that the portions of organic matter bonded to inorganic surfaces by cation bridges have similar contents of polyvalent cations. The explanation for the different levels of pyrophosphate extractable Al and Fe, and for the different levels of organic matter must therefore be sought in the kinds and amounts of inorganic surfaces available for organic matter adsorption.

Negatively charged, amorphous aluminosilicates appear to offer the chemically most favorable surfaces for organic matter adsorption. Some of the proposed organo-mineral bonds (e. g., cation bridges, ligand exchange) depend strongly on the nature of the inorganic surfaces. Hence, it is possible that an increased availability of a particular type of surface could result in an increased portion of the organic matter adsorbed by the corresponding type of bond. It can be inferred that amorphous aluminosilicates enhance all of the proposed bonds (except anion exchange) due to their negative charge, their

aluminous surface, and their high specific surface area. This would explain the levels of pyrophosphate extractable Al and Fe in coastal soils containing amorphous aluminosilicates. It also offers a partial explanation for the high organic matter accumulations in coastal soils, although many questions remain regarding quantitative chemical determinations as well as biological and climatic influences.

The oxalate and dithionite extraction data were difficult to interpret due to the many uncertainties regarding their specificity to extract amorphous oxides, and amorphous plus crystalline oxides of Al and Fe. However, dithionite in conjunction with pyrophosphate appears to be useful for the chemical identification of spodic horizons.

The taxonomy of the soils used in this study remained unchanged, except for Nehalem and Knappa. The Nehalem series is officially classified as a Fluventic Haplumbrept. The Nehalem profile sampled for this study was found to be a Fluventic Hapludoll. The Knappa series is officially classified as a Pachic Haplumbrept. All the taxonomic data for the Knappa profile (except DTA-data which were not determined) show that it is a member of the Typic Dystrandept subgroup.

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