

MINERALOGICAL, CHEMICAL, AND
FERTILITY RELATIONSHIPS OF
FIVE OREGON COASTAL SOILS

by

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MINERALOGICAL, CHEMICAL, AND FERTILITY
RELATIONSHIPS OF FIVE OREGON COASTAL SOILS

INTRODUCTION

Oregon's coastal soils have developed under somewhat uncommon climatic conditions. The rainfall in this area varies from 75 to 100 inches per year but is concentrated, primarily, in the winter months with very little summer precipitation. The marine climate provides relatively mild temperatures throughout the year. This combination of wet winters with little or no frost and dry cool summers has resulted in a dense vegetative cover on both the dominantly sedimentary upland soils and the alluvial soils of the valley floors and terraces. The concentration of rainfall in the winter has caused extensive leaching while the dry summers have restricted the decomposition of organic matter.

The action of these climatic factors on this group of sedimentary and alluvial soils has generally resulted in: 1) high organic matter levels; 2) very acidic conditions with a relatively high degree of aluminum and/or hydrogen saturation of the exchange complex; 3) a low level of bicarbonate extractable phosphorus; and 4) relatively low exchangeable potassium values.

Prior soil fertility research and county agent field demonstration plots had indicated the need for lime and

phosphorus for efficient production of legume-grass pastures. Some indication of potassium response had been obtained at the John Jacob Astor Experiment Station. Greenhouse experiments with certain of these soils resulted in abnormal clover growth after two or three harvests had been taken.

Information from the above sources provided a basis for selecting fertilizer variables and rates for a series of fertilizer experiments established under an expanded soil fertility research program in the coastal area in 1956.

An adequate interpretation of experimental results requires that they be explainable. It appeared that a study of the clay mineralogy of these soils would supplement the fertility investigation of these soils. Such a study would be useful in 1) explaining, at least partially, the soil chemical properties and fertility responses of these soils; and 2) extending the applicability of the results of these field experiments to other related soils.

Although beyond the scope of this study, it is nevertheless realized that the relatively high (8 to 20 percent) organic matter content of these soils undoubtedly plays an important role in their chemical properties and fertility responses. Unfortunately, procedures have not yet been developed that adequately evaluate the role of organic matter

in soil chemical properties.

The objectives of this investigation may be stated as follows: 1) to characterize chemically and mineralogically the inorganic portion of profile samples from five coastal soils; 2) to relate, in so far as possible, the chemical properties and fertility responses to the clay mineralogy of those soils.

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W. L. BROWN Paper

LITERATURE REVIEW

Introduction

Properties of individual soil minerals, and less commonly of mixtures of known mineral composition, have been studied for many years. One example of the usefulness of soil mineralogical information is the prediction and/or explanation of potassium and ammonium fixation by vermiculite and, to a lesser extent, by certain other minerals. Another use often made of mineralogical data is that of liming soils to different degrees of base saturation depending on whether they are kaolinitic or montmorillonitic.

To assist in interpretation of the chemical properties and fertility responses of the soils used in this study, some of the more pertinent investigations are reviewed in the following section. Inasmuch as the gross chemical properties of the layer silicates are fairly well known they are treated rather briefly.

Contribution of Layer Silicates to Soil Chemical Properties

The outstanding chemical property varying among the layer silicates herein considered (montmorillonite, vermiculite, chlorite, illite, and kaolinite) is cation exchange capacity. Ranges of values in me./100 g. are as follows: montmorillonite, 80 to 150; vermiculite, 100 to 150;

chlorite, 10 to 40; illite, 10 to 40; and kaolinite, 3 to 15 (23).

The site of approximately 80 percent of the base exchange capacity of montmorillonite is considered to be between the crystal layers rather than on their edges as would be the case for non-expanding layer silicates. The exchange sites on the crystal edges are due to oxygen which has one valence that is not satisfied by the crystal per se. The oxygen of the crystal edges forms a stronger bond with hydrogen than the alkali and alkaline earth cations. The same mono- and divalent cations are more strongly bonded on the interlayer exchange sites of the expanding clays than is hydrogen. This, then, explains why a montmorillonitic soil must normally be limed to a higher base ^{1/} saturation than kaolinitic and illitic soils (i.e., non-expanding structures) to provide the same availability of calcium for plant nutrition.

Chu and Turk (15) used pot cultures of layer silicates to determine the optimum degree of base saturation and found that the growth of plants was more closely related to the degree of base saturation than the total supply of exchangeable bases. They found a nearly linear relationship between yield and degree of base saturation for plants

^{1/} As used in this thesis, exchangeable bases refers to the sum of the exchangeable calcium, magnesium, potassium, and sodium present on the exchange complex.

grown in montmorillonite. In a kaolinitic media, yield increases were noted only up to 40 percent base saturation. The results for an illitic soil were intermediate, i.e., the highest yield was obtained with a base saturation of 75 percent.

Mehlich and Colwell (41) adjusted whole soils to percent calcium saturations of 20 to 80 percent. They also adjusted them to equivalent cation exchange capacities by dilution with quartz sand. The results obtained were identical with those of Chu and Turk (15). With a soil containing roughly equal quantities of montmorillonite and kaolinite, maximum yield was reached at 60 percent calcium saturation.

The minerals present in soils are also markedly different in elemental composition. Thus, the mineral suite present determines the potential fertility of a soil. Since the weathering of minerals in soils is a relatively slow process, there is a small but continuous supply of nutrient elements released. It may, therefore, be of some interest to consider briefly what nutrients may be supplied by clay minerals. Illites (micas) are very important sources of potassium. Potassium is released by feldspars though at a much slower rate (20). Grim (23) reports that K_2O percentages of illite range from 3 to 8 percent. The montmorillonite analyses he has tabulated show that only

fractional percentages of K_2O occur in montmorillonites or in the kaolin minerals. Appreciable quantities of magnesium are released by weathering of both vermiculites and chlorites. Only fractional percentages of calcium are contained in the vermiculites, chlorites, illites, kaolin minerals, and in most montmorillonites. A few of the montmorillonite analyses listed by Grim (23) show CaO percentages of up to 3. The plagioclase feldspars also contain appreciable amounts of calcium.

The ability of vermiculite to fix large amounts of ammonium and/or potassium is a characteristic and important property. This property is usually exhibited to a lesser degree by illite and still less by montmorillonite. The ability of the expanding layer silicates to fix potassium and ammonium is a function of the charge density of both the octahedral and tetrahedral layers, though the latter is more important (52, 4). Certain western Oregon soils have recently been found to fix large quantities of NH_3 . The fixation capacity of both the mineral and organic portions were important (12).

A relationship has been shown to generally exist between the release phenomena of potassium and the presence of a 10 \AA layer silicate in a number of soils (20).

Contribution of Amorphous and Hydrous Oxides of Silicon, Aluminum, and Iron to Soil Chemical Properties

It is first necessary to consider briefly the terminology of the amorphous and/or hydrous oxides of iron, aluminum, and silicon. The term allophane has been applied to a variety of materials. Ross and Kerr (46), White (56), Jaffe and Sherwood (29) and numerous others have used this term for geological specimens of amorphous aluminosilicates containing variable contents of phosphorus. In Japan and New Zealand, the term allophane is used for amorphous aluminosilicates of soils which have varying degrees of iron admixed. Recently, allophane of the type occurring in Ando soils (2), which was believed to have formed as a result of coprecipitation of silicon and aluminum, has been defined on the basis of a property, namely, the ability to exhibit very different cation exchange capacities as a result of pretreatment with an acid on the one hand or an alkali on the other hand. Fieldes (19) has distinguished allophane A from allophane B on the basis that a considerable amount of silica is discrete in allophane B as evidenced by differential thermal analysis. Additionally, he considers that the degree of aluminum-silicon bonding is less in allophane B.

At least some of the material referred to in soil science literature as sesquioxides would be allophane by one or more of the criteria. Until it can be ascertained

that the geological specimens are in fact the same type of material as "Ando type allophane" and as the allophane A and B of New Zealand soils, it would appear to be best to avoid using the term allophane. Therefore, these amorphous hydrous oxides are subsequently referred to in this dissertation as amorphous materials as the information is not presently available that would justify greater specificity in terminology.

A number of New Zealand and Australian workers have found that amorphous aluminosilicates and hydrous oxides of aluminum and iron have a very definite effect on soil chemical and physical properties. Phosphorus fixation and subsequent low degree of availability is a serious problem in many agricultural areas of the world. In New Zealand, this fixation has been shown to be primarily due to reactions with hydrous sesquioxides. Phosphorous fixation may also proceed at a much slower rate due to decomposition of structural aluminum and iron (43, 36). Wada (51) has recently shown that the reaction between allophane and phosphorus at pH 4 is very rapid and results in large quantities of phosphorus being fixed within 24 hours. Hexagonal crystals, forming from allophane to which phosphorus had been added, were noted with the light microscope after 3 weeks. The crystals were found to be taranakite. The remarkable rapidity of the reaction was considered to be due to the

high specific surface of allophane.

Chao (14) found that latissolic soils (of Oregon) show a marked capacity for retention of sulfate ions. Whereas the sulfate ion was reasonably mobile in most soils, it moved only slightly as a result of leaching in soils high in sesquioxides.

Wells (55) found molybdate ion retention by New Zealand soils to be primarily due to allophane and hydrous aluminum and iron oxides, with the iron oxides being the soil component which rendered the molybdenum unavailable. In molybdenum fixation studies, phosphate was found to be more strongly adsorbed than molybdate (55). These results were, in effect, predicted by the results of Fieldes (18) who reported that under soil conditions, the hydrous oxides of iron and aluminum tend to behave as positive colloids and hence would be active in phosphate and molybdate fixation.

Amorphous materials show remarkable adsorptive effect for metal cations, an effect which gives soils containing them an apparently high cation exchange capacity. Though in some cases cation exchange capacities are relatively low, where crystalline clay minerals are very sparse (17), the magnitude is usually from 30 to 90 me./100 g. Tanada (49) found cation exchange values generally of 30 to 40 and up to 50 and 60 me./100 g. in Hawaiian soils where 2:1 layer silicates were present in only small quantities. Kanno (32)

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found cation exchange capacities of 54 and 26 me. for the A horizons of two allophanic soils and 80 and 75 me. for their less than 1 micron separates. He also reported that the exchangeable bases were usually less than 5 me./100 g. This low degree of base saturation was associated with large amounts of exchangeable aluminum. Aomine and Yoshinaga (3) report cation exchange capacities of 23 to 57 me./100 g. for volcanic ash soils containing allophane as the major clay constituent. Harada (26) reports a considerable difference in cation exchange capacity of allophanic clay depending on whether BaOAc or BaCl₂ was used in the determination. For samples of 32 and 15 percent allophane, the exchange capacities were 30.7 and 54.4 me./100 g. with BaOAc and 3.3 and 6.0 me./100 g. with aqueous BaCl₂. No explanation for this phenomenon was offered.

Birrell and Gradwell (7) report that soils containing allophane and amorphous oxides give cation exchange values which vary considerably with the concentration of leaching solution, the cation, the volume of washing alcohol, and the water content of the alcohol. They concluded that this indicated some adsorption mechanism rather than an exchange process. The ease with which allophanic clays lose their metal cations as a result of leaching with water had been demonstrated earlier by Birrell and Fieldes (6). They leached 0.5 g. of allophane with 250 ml. of water and

removed about half of the adsorbed sodium. Thus, the water content and amount of alcohol used in washing would control the amount of hydrolysis.

Another factor influencing the cation exchange capacity of amorphous materials is that of pH. In 1931, Mattson (39) reported that the exchange capacities of artificial aluminum and silicon coprecipitates determined at pH 7 were different depending upon whether the precipitates were first treated with an acid or base. Birrell and Fieldes later made a similar observation with an allophanic clay. This phenomenon has recently been observed again by Aomine and Jackson (2) and subsequently developed into a method for determining allophane of "the type occurring in Ando soils".

Japanese Ando (an meaning dark and do meaning soil) soils may have a bulk density as low as 0.4 and organic carbon contents up to 30 percent (32).

Packard (44) has noted that in the pumice soils of New Zealand, the presence of allophane renders mechanical analysis (using hydrogen peroxide pretreatments and sodium hexametaphosphate as the dispersing agent) difficult and causes poor reproduceability. In one case he found by surface area measurements that there should have been 11.6 percent clay, but only 4 percent was found by mechanical analysis in the clay separate. The remainder was distributed in the silt fraction. Sixty percent of the allophane was in the 2 to

20 micron fraction and 30 percent in the 20 to 70 micron fraction as determined by surface area measurements.

Birrell (5) has made a similar observation and additionally has noted that the presence of much aluminum or iron oxides made the dispersion of allophanic soils even more difficult. Kanno and Kawano (33) report that in the case of volcanic ash soils (presumably all containing amorphous aluminosilicates) each sample should be pretested to determine whether an acidic or alkaline dispersing medium produces maximum dispersion.

Because of the extremely fine particle size and hence large surface area, amorphous materials give soils a large water holding capacity (5).

EXPERIMENTAL

Materials

Field Experiments

A fertility experiment was established on Astoria soil on the John Jacob Astor Branch Experiment Station in the summer of 1956. The indicator crop was a New Zealand white clover (Trifolium repens)-orchard grass (Dactylis glomerata) mixture. This site presented a number of advantages. One advantage was the assistance and interest of Mr. Herb Howell, Station Superintendent. This site was also representative of the most extensive coastal soil. Another advantage was that irrigation was possible. Yield data were obtained in 1957, 1958, and 1959.

With the assistance of Dr. Ellis Knox and Soil Conservation Service personnel, eight additional coastal soils were selected on the basis of agronomic importance. Samples from these soils were collected in Clatsop, Tillamook, Lincoln, and Coos Counties. These samples were characterized by cation exchange capacity, exchangeable cations, pH, lime requirement, and available phosphorus. This survey indicated something of the range in values that might be expected in these soil series (see appendix I).

Good experimental sites of both Nehalem and Tillamook soils were found on the environs of the Tillamook Naval Air

Force Base, east of the city of Tillamook, Oregon. Thus, in March, 1958, plantings of New Zealand white clover-orchard grass-perennial rye grass (Lolium perenne) were made on these two soils. Yield data were obtained from both experiments in 1959 and from the Tillamook location in 1960.

Profile Samples

Profile samples were taken from the three field experimental sites. Profiles of a Winema soil near the city of Tillamook and from a Clatsop soil at the John Jacob Astor Branch Experiment Station were also sampled. Profile descriptions of the profile samples at the field experimental sites may be found in appendix II. Table 1 gives some general information about these soils.

Reference Minerals

Mr. Melvin Williams, Territorial Soil Scientist of Hawaii, kindly supplied an undried Hilo subsoil sample which was believed to be high in allophane (see appendix III for a general description).

A less than 20 micron size fraction from a Japanese volcanic ash soil was kindly supplied by Dr. Shigenari Aomine of the Faculty of Agriculture of Kyushu University, Fukuoka, Japan.

Montmorillonites 11 and 24, kaolinite 4, illite 35,

Table 1. Classification of Soils With Regard to Great Soil Group, Parent Material, Drainage, and Vegetation

Soil Series	Great Soil Group	Parent Material	Natural Drainage	Natural Vegetation
Astoria	Brown Latasol ^{2/}	sedimentary residium	good	conifer forest
Nehalem	Alluvial ^{3/}	recent alluvium	good	conifer forest
Tillamook	Ando ^{3/}	old alluvium	good	shrubby grassland
Clatsop	Alluvial	recent alluvium	very poor	marsh
Winema	Ando ^{3/}	sedimentary residium	good	shrubby grassland

^{2/} This name has been used locally and is defined by Ellis Knox and Melvin Williams (manuscript in preparation).

^{3/} While not derived principally from volcanic ash as are the Japanese Ando soils, these soils appear to be quite similar to the Japanese Ando soils.

prochlorite 6, and a vermiculite ^{4/} were from Ward's Natural Science Establishment, Inc.^{5/} The first 3 minerals were ground in a mortar to pass a 40 mesh sieve while the prochlorite and vermiculite were ball milled for a number of hours and then passed through a 1 mm. sieve.

Profile Characterization

Chemical Analyses

The procedures used were those of Oregon State College Soil Testing Laboratory (1).^{6/} Lime requirement was determined by the Woodruff method. Available phosphorus was estimated by extraction with sodium bicarbonate and the color developed with ammonium molybdate. Cation exchange capacity was determined by saturating the exchange complex with ammonium, displacing with hydrochloric acid, and by determination of ammonium displaced. The extract from the ammonium acetate wash was used for determination of exchangeable sodium, potassium, calcium, and magnesium on a Beckman Model B flame photometer. Total salts were determined by measuring the conductivity of the extract of a 1:1

^{4/} This sample contains only minor amounts of discrete vermiculite as evidenced by a weak 14 Å peak. This material gave a strong 12 Å peak and a very strong 26 to 27 Å peak.

^{5/} P.O. Box 24, Beechwood Station, Rochester 9, New York.

^{6/} Most of the routine soil chemical analyses were performed by the Soil Testing Laboratory, Oregon State College.

soil:water paste. Organic matter was determined by the Walkley-Black wet digestion procedure. Total nitrogen was determined by the Kjeldahl method. Boron was extracted by refluxing with distilled water and was determined by the intensity of the color developed with curcumin.

pH was determined in 1:1 water suspensions and in 2:1 suspensions of 1 N KCl. Five g. samples were weighed into soufflé cups and 5 ml. of water added, followed by stirring. After a minimum of 30 minutes the samples were again stirred, and the pH read with a Beckman model G pH meter as soon as a stable reading was obtained, i.e., 3 successive readings within ± 0.02 pH units. Subsequently, 5 ml. of 2 N KCl were added to the cup with stirring. The samples were thus 1 N with respect to KCl added. After 30 more minutes, the samples were stirred and the pH again recorded.

Physical Analyses

Mechanical analyses of 10 g. profile samples were performed ^{7/} by the pipette method using samples prepared as described in a later section on sample pretreatment. A solution of Na_2CO_3 , (2 g. Na_2CO_3 per 18 l. of water) buffered at pH 9.5, was used as the dispersion medium in conjunction with an air jet dispersion apparatus ^{8/} as

^{7/} These analyses were performed by the Soil Physics Laboratory, Oregon State College.

^{8/} Purchased from Testlab Corporation, 2734 North Laramine, Chicago 39, Illinois.

modified by Chu and Davidson (16). It was determined experimentally that the maximum volume that could safely be used in the 1205 ml. hydrometer cylinders without danger of loss past the baffles during the agitation was about 200 ml. of Na_2CO_3 -soil suspension. Each sample was split into two cylinders and dispersed for 5 minutes at 25 p.s.i. air pressure. The two portions were sieved through a 300 mesh sieve into a single cylinder which was filled to the 1130 ml. mark with the Na_2CO_3 solution. The sieve was then washed with sufficient distilled water to bring the suspension level up to the 1205 ml. mark. The cylinders were then immersed in a 20°C . constant temperature bath over night. After mixing, aliquots were withdrawn at suitable times for estimating the less than 50 (52.8 seconds/12 cm.), 20 (5.6 minutes/12 cm.) and 2 (6 hour 8 minutes/8 cm.) micron fractions. The sediment remaining on the sieve was then dried and again sieved to remove the coarse silt remaining on the sieve. The weight of the material passing the sieve was added to that of the 50 to 20 micron fraction calculated from the pipette analysis in order to arrive at the total weight of this fraction. The sample weight used for calculating the relative proportions of the various size fractions was taken as the sum of the various size fractions.

Moisture retention was determined by the soil physics

laboratory using a pressure membrane apparatus.

Dilute Equilibrium Extracts

It was desired to characterize the experimental sites with respect to the availability of Ca+Mg as well as potassium. Information was obtained on the effect of both lime and potassium fertilization rates by sampling the pertinent plots and then compositing replications of the same treatments after the samples were ground to pass a 1 mm. sieve. These composited samples were then subsampled to provide another composite which was used for the determination of cation exchange capacity.

The method used was that of Webster and Harward (54) as adapted by Chao (13) for his studies with reference minerals. Sufficient amounts of each sample were weighed into 125 ml. Erlenmeyer flasks to provide an exchange capacity of 0.5 me. Fifty ml. of water was added to each flask from a fast delivery 250 ml. buret. The flasks were then stoppered and shaken for one hour, then for an additional 30 minutes while bubbling compressed air through the suspension from capillary tubes fitted with stoppers. The samples were next centrifuged in a Servall SS-1 supercentrifuge at 12,500 r.p.m. (relative centrifugal force of 18,800) for 12 to 15 minutes. The supernatant was then filtered through Whatman number 5 filter paper into 50 ml. beakers. The

extracts were again equilibrated by bubbling compressed air from capillary tubes through them for 20 minutes before determining their pH on a Beckman model G pH meter. A capillary tube extending slightly below the electrodes was taped to the door of the electrode compartment. Compressed air was bubbled through the sample at a rate of 1 to 2 bubbles per second while the pH was being read. With a slower rate of gas flow the pH values would drift while faster flow rates caused excessive fluctuation of the pH meter. The electrode cavity door was held tight against the capillary tube and as nearly closed as possible with masking tape.

Calcium and potassium were determined on the same extract on the same day using the ethylenediaminetetraacetate titration method (50) for calcium and the flame photometer for potassium.

Calcium concentration in equilibrated extracts, as a function of percent calcium saturation, was also studied on an undried Hilo subsoil sample. The technique used for the Hilo differed only slightly from that just described. The 2.91 g. subsamples (1.075 g. on oven dry basis) were weighed into 125 ml. Erlenmeyers as quickly as possible on a torsion balance to minimize moisture evaporation. The presence of pumice fragments made the extraction of representative subsamples difficult. Approximately 0.5 g. of filter pulp was added to facilitate washing. $\text{Ca}(\text{OH})_2$ was

added to the Hilo subsamples to give a range of Ca from 0.64 (natural Ca+Mg saturation) to 400 percent Ca saturation. The water present in the sample itself (1.9 ml.) was taken into account in adding the water.

Mineralogical Studies

Sample Pretreatments

Five g. of air dry soil were accurately weighed out into 220 ml. polyethylene cups,^{9/} washed twice with N NaAc adjusted to pH 5, and then transferred to 400 ml. beakers. Five ml. of 30 percent H₂O₂ were added to the beaker which was then covered with a watch glass and allowed to react over night. The following morning the pH was adjusted to approximately pH 3.5 with HCl using bromophenol blue indicator. The beakers were then transferred to a steam bath and digested for about 1 hour or until evaporated nearly to

^{9/} The 220 ml. polyethylene centrifuge cups were made by cutting off the top of 60 x 125 mm. polyethylene 250 ml. bottles just below the cap so as to leave a 1 1/4 inch opening. A suitable pouring lip was made via a heated glass rod. These centrifuge cups have a number of advantages, specifically, they are: non-breakable; not affected by boiling water; not damaged by drying at 95-100°C.; are sufficiently translucent to show the suspension level; and may be permanently graduated with various marking pens. Thus, the cups can be used throughout the common sample treatments, prior to size segregation, if a defoaming agent is used during organic matter removal as noted by Kittrick (35).

a paste. The beakers were then removed from the steam bath and allowed to at least partially cool before adding 10 ml. of H_2O_2 . The digestion, evaporation, cooling, and H_2O_2 additions were continued until a total of 70 ml. of 30 percent H_2O_2 per 5 g. sample had been added.

The organic matter free samples were transferred quantitatively to 220 ml. centrifuge cups and centrifuged using 5 ml. of saturated NaCl to promote flocculation. Each sample was washed twice with 30 ml. of 1 N NaOAc and once with absolute methanol. The purpose of the washings was to facilitate subsequent dispersion by removal of soluble organic matter not completely oxidized by the H_2O_2 treatments, to remove exchangeable divalent cations, and, lastly, to remove any carbonates that might be present.

Free iron oxides were removed essentially as described by Jackson (28, p. 57). A more thorough removal was obtained by increasing the amount of dithionate to 9 g. per 5 g. of soil and carrying out four extractions. To the washed, organic matter-free soil in the polyethylene centrifuge cup, 35 ml. of 0.3 N sodium citrate were added. This was buffered at pH 7.3 with 5 ml. of M $NaHCO_3$. The sample was heated on a steam bath or in a water bath for 15 minutes (this gave a temperature of 68-72°C.). The $Na_2S_2O_4$ was added and the sample brought into suspension

with a power stirrer, ^{10/} after which the sample was returned to the bath for just 15 minutes. After adding 10 ml. of saturated NaCl to promote flocculation, the samples were centrifuged. Four such extractions and a final wash with the sodium citrate were made with the supernatant being decanted into volumetric flasks and saved for iron analysis.

It was deemed advisable to use Jackson's (28, p. 73) 2 percent boiling Na_2CO_3 treatment to obtain a more nearly complete dispersion, since these soils were suspected of containing amorphous aluminum and silicon oxides which act as cementing agents.

The samples were transferred with approximately 200 ml. of 2 percent Na_2CO_3 solution to 250 ml. nickel crucibles. The suspension was brought to a boil as quickly as possible with a gas burner, then boiled for exactly 5 minutes, poured back into the polyethylene cups and centrifuged again. The sediment was washed twice with 50 ml. of the Na_2CO_3 solution.

Particle Size Separation

Particle size separations at 50, 20, 2, 0.2, and 0.08 microns effective spherical diameter were made as described

^{10/} A malt mixer of the type commonly used for mechanical analysis was adapted by replacing the metal blade with a rubber policeman.

by Jackson (28, pp. 101-164) with one exception. Since a continuous flow centrifuge was unavailable it was not feasible to carry out the clay size separations by progressing to successively smaller particle sizes.

The boiling Na_2CO_3 treated sample was brought into suspension in the polyethylene cups and allowed to settle 10 seconds per inch of depth, then decanted onto a 50 micron (300 mesh) sieve suspended above a 600 ml. beaker. The material remaining on the sieve was washed vigorously with pH 9.5 Na_2CO_3 solution from a wash bottle, then given a final wash with acetone. After settling for 1 hour or more, the supernatant in the beaker was decanted into a 2 l. flask. The sediment was transferred to 100-ml. tall-form beakers using pH 9.5 Na_2CO_3 buffer solution. The beakers were filled to the 5 cm. mark (or higher where necessary to complete the transfer) and allowed to settle for 5 minutes per 5 cm. before decanting into the 2 l. flask. The sediment was resuspended five times and allowed to settle for periods of 3, 2, 2, 2, and 2 minutes respectively before successive decantations. The last two decantations were made with distilled water. The 20 to 2 micron fraction was recovered by centrifuging the suspension obtained from the coarse silt separation for 5 minutes at 2,000 r.p.m. (relative centrifugal force of 300) in a number 2 international centrifuge and again decanted into 2 l. flasks.

The sediments were resuspended with pH 9.5 Na_2CO_3 solution to the 7 cm. mark and centrifuged at 750 r.p.m. (relative centrifugal force of 53.4) for 3.80, 2.84, 2.70, and 2.70 minutes respectively. Finally, they were resuspended twice more in water and centrifuged for 2.70 minutes prior to each decantation.

To the less than 2 micron suspension, sufficient reagent grade NaCl was added to flocculate the suspension. Warming in a water bath speeded up the process. The clear supernatant was siphoned off and discarded. The sediment was transferred, again with pH 9.5 Na_2CO_3 solution, to 50 ml. centrifuge tubes and centrifuged in a Serval Superspeed SS-1 centrifuge at 12,500 r.p.m. (relative centrifugal force of 18,800) for 12.67 minutes (21°C.). The first wash was discarded as was the second one, if clear. Six further washings were usually sufficient to remove the less than 0.08 micron fraction as evidenced by clearness of the suspension after centrifuging. Each sample was decanted into a volumetric flask which was made up to volume when the separation was complete. The suspensions were stored in 250 or 500 ml. Erylenmeyers.

The remaining size separation was made with the Serval Superspeed centrifuge at 6,000 r.p.m. for 8.3 minutes (21°C.). Five washings were usually sufficient for separation at 0.2 microns.

Suspension densities were determined by weighing oven dried aliquots. The less than 0.08 and the 0.2 to 0.08 micron fractions were washed twice with 0.05 N HCl and once with acetone prior to drying to remove the Na_2CO_3 dispersion agent.

X-ray Diffraction

X-ray diffraction analyses were performed with a North American Philips Norelco unit equipped with a Geiger-Muller tube and a Brown recorder. Cu K-alpha radiation in conjunction with power settings of 20 millamperes and 40 kilovolts were used exclusively. Except for special cases a scanning speed of $1^\circ 2\theta$ was used.

Random powder patterns were run on selected sand and silt fractions using a $1\frac{1}{2} \times 1\frac{3}{8} \times \frac{3}{16}$ inch aluminum holder having a $\frac{26}{32} \times \frac{13}{32} \times \frac{3}{32}$ inch sample cavity closed on the bottom with a microscope slide glass cover. A reasonably level surface was obtained by smoothing with the wide side of a microscope slide. For these analyses, divergence, scatter, and receiving slits of 1° , 0.006° , and 1° were used.

Parallel orientation of the clay fractions was obtained by depositing them on glass microscope slides. The sediment was restricted to an area of 1 square inch. For these analyses, divergence, scatter, and receiving slits of $1/4^\circ$,

0.006^o, and 1/4^o were used. The preparation of the slides is described below.

Four aliquots of 10 mg. each were withdrawn from each of the size fraction (2-0.2, 0.2-0.08, and less than 0.08 microns) suspensions of the various profile samples and transferred to 50 ml. centrifuge tubes. Two aliquots were washed twice with 20 ml. of N KCl, then twice with water, the other 2 aliquots being washed with N CaCl₂ and then with water. The first water wash was with 20 to 30 ml., but the second water wash was with only 10 ml., so that the sediment was concentrated at the bottom of the tube. This facilitated the resuspending of the sediment in a minimum of water. After the final wash, the tubes were decanted and stoppered until the sediment could be transferred to slides. The sediment was resuspended by use of a variable speed stirrer equipped with a rubber policeman. The variable speed stirrer was found to be essential to this operation. The advantage of the power stirrer is that it is self cleaning, whereas, with a rubber policeman fitted to a stirring rod, excessive quantities of water are often required to clean the policeman. With this technique, it was possible to suspend the sediment with as little as 3 to 5 drops of water. The suspension was transferred to the appropriately marked slide with an eye dropper drawn out to a capillary tip. Two or three more drops of water were

added to the tube to rinse the tube and stirrer, and then added to that already on the slide. Using this technique, it was possible to transfer quantitatively the sediment to a slide in approximately 1 minute.

After obtaining diffraction patterns of the duplicate calcium and potassium saturated slides, one of the calcium slides was glycolated while one of the potassium slides was heated to 500°C. The calcium and potassium duplicate slide having the most intense reflections in the 14 to 17 Å region was selected for the glycolation and heat treatment respectively. Glycolation was done by the method of Brunton (10). The 500°C. heat treatment was carried out only in those cases where a 14 Å peak remained after the ethylene glycol treatment.

The method of Brindley and Youell (9) was used to dissolve the chlorite in certain samples. This consisted of adding 30 ml. of 10 percent HCl to centrifuge tubes containing 10 mg. of clay separates. The tubes were then immersed in boiling water for two hours, centrifuged, decanted, calcium or potassium saturated, and deposited on glass slides for X-ray diffraction analysis.

Cation Exchange Delta Value

Aomine and Jackson (2) have recently reported a method of identifying allophane of the type occurring in Ando

soils of Japan, utilizing the differential cation exchange capacity of inorganic amorphous constituents incurred by acidic or basic pretreatments. This method was used to evaluate the presence of this type of allophane in these soils.

The samples were pretreated as described in the sample pretreatment section with the exceptions noted below. During free iron oxide removal, 10 ml. of acetone were used instead of saturated NaCl to promote flocculation. Subsequent to free iron oxide removal, all of the samples were washed twice with a 3:1 mixture of acetone and absolute methanol, then once with acetone. After the boiling Na_2CO_3 treatment, the samples were similarly washed. The initial wash with 1:1 mixture of acetone and methanol as recommended in the published method did not provide complete flocculation, so a 3:1 mixture was substituted.

Four subsamples of one hundred mg. each of oven dry material were weighed out into 50 ml. centrifuge tubes. Five ml. of 2 percent Na_2CO_3 were added to 2 of the samples and the tubes placed in boiling water for 1 hour. Five ml. of N NaOAc buffer solution of pH 3.5 were added to the other 2 tubes which were then immersed in boiling water for 15 minutes. Each subsample was washed as follows: 5 times with 20 ml. of N KOAc; 6 times with 95 percent methanol; and 5 times with 20 ml. of neutral N NH_4OAc . The NH_4OAc

washes were decanted into filter funnels draining into 100 ml. volumetric flasks and the potassium determined on a Beckman DU flame photometer. The supernatants were filtered to avoid the possibility that a flake of clay might clog the DU burner and also to remove bits of filter pulp which was added to some of the higher sand content samples to bond the sediment together while decanting. Where the solutions were to be held for a day or two, a drop of CCl_4 was added to each volumetric flask to prevent microbiological growth.

Sodium Hydroxide Solubility

Alkaline treatments (NaOH or Na_2CO_3) have been used for a number of years for "cleaning" soil clays. However, it is only recently that the variables have been scrutinized and its effect on the layer silicates evaluated (27). This method was used to determine the amounts of amorphous inorganic material in the soils studied.

Approximately 0.20 g. of the samples prepared as described in the preceding section for cation exchange delta values were weighed out into previously tared weighing bottles. The bottles plus samples were then oven dried, removed to a dessicator to cool, and weighed as accurately as possible. The samples were then transferred to 250 ml. nickel crucibles using a total volume of 150 ml. of 0.5

N NaOH. The suspension was brought to a boil as quickly as possible, then boiled for 2.5 minutes. The suspension was then centrifuged in the supercentrifuge, washed twice with 30 ml. of 0.05 N HCl and 10 ml. of acetone to ensure flocculation while removing the NaOH, then once with 3:1 acetone:water mixture. The sediment was then transferred to the weighing bottles, dried and weighed. The results are reported as percentage weight loss.

Differential Thermal Analysis^{11/}

The equipment used was that of the Analytical Division of the Albany Branch of the U. S. Bureau of Mines. This apparatus has been described in detail by Kauffman and Dilling (34). The vertically mounted sample holder is a 1 1/2 inch long by 1 inch wide and 4/8 inch deep nickel block with the ends slightly rounded. The temperature control thermocouple is located in a 1/4 inch deep hole in the center of the under side of the sample holder. The chromel-alumel thermocouples are positioned by 2 hole 1/4 inch O. D. alundum tubes which fit snugly into the lower portion of the four 1/4 inch I. D. sample cavities so as to leave an effective sample cavity depth of 6 mm. The heating rate was found to be only approximately linear with an average

^{11/} Appreciation is expressed to the Analytical Section of the Albany Branch of the U.S. Bureau of Mines for making these facilities available.

rate of 8.6° /minute. The heating rate for this instrument given by Kauffman and Dilling was 10 to 12° /minute. The differential thermograms were recorded by a Brown Electronik Multipoint Recording Potentiometer with a chart speed of 0.164 inches/minute.

Portions of the samples prepared for cation exchange capacity delta values were used for differential thermal analysis. Because of the limited amount of samples remaining from other analyses, the samples were diluted with 600 mesh alundum previously calcined at 800°C . A portion of the same alundum was used for filling the reference thermocouple cavity. The samples were packed into the cavities by use of a $1/16$ inch wire with a flat end until the sample level was above the thermocouples, then a $7/32$ inch O. D. steel rod was used. The rod was not pressed down, but sample compaction was only by the rod weight as it was vibrated slightly. The samples were equilibrated over saturated calcium nitrate previous to performing the differential thermal analysis, as recommended by Mackenzie and Mitchell (38).

RESULTS AND DISCUSSION

Field Experiments

Astoria

This section describes the response of the legume-grass mixture to the various fertilizer treatments. The interpretation of these results will be considered further in the general discussion section to follow.

The most important fertilizer response on this soil was to potassium. These responses were found to be significant ^{12/} at the 1 percent confidence level in both 1957 and 1958 (the analysis of variance for the 1958 yield data is presented in appendix VI). In 1957, yield increases due to 200 pounds of potassium were 1300 pounds per acre (dry weight) and 2400 pounds per acre in 1958 (appendix V). In 1957, potassium foliar deficiency symptoms were noted throughout the season in plots receiving 100 pounds of K_2O per acre and some foliar deficiency symptoms were noted at the 200 pound rate at the time of the third and fourth harvests. The following year the potassium fertilizer was applied in three installments. The first application was made early in the spring with additional applications after the second and fourth harvests (5 harvests were made).

Yield increase due to 24 tons of lime per acre was
12/All statistical analyses were performed by the Agricultural Experiment Station Statistical Service, Oregon State College.

2600 pounds per acre in 1957 and 1700 in 1958. The second year a lower lime rate was sufficient for maximum production. The lime response was significant at the 5 percent level in 1957 but not in 1958.

Yield increases from phosphorus, magnesium and sulfur were not significant in either year.

Analysis of the third year's harvest data (2 cuttings) showed results similar to the preceeding year, i.e., potassium response was significant at the 1 percent level while responses to lime or phosphorus responses were not significant. There appeared to be no interaction effects.

Field observations have yielded some interesting information in addition to the yield data. One of these observations was that an excellent stand of both grass and clover was initially obtained. This is of importance in considering fertilizer responses because in cases where seedling vigor is low and a poor initial stand obtained, the first year's yield data may not represent the true fertility status of the soil. In the case of this experiment, there was little change in yield response between years. It has, however, been observed that the stand of clover has practically disappeared from the plots not receiving the potassium. A somewhat unusual situation was the increased vigor and stand density of the orchard grass on the limed plots. This was particularly noticeable the first year that the

plots were harvested.

The data presented in appendix XI shows the increase in the nitrate production during a 2 week incubation period as a function of lime rate. The increase is particularly marked at the high lime rate (24 tons per acre). These samples were taken subsequently to the third harvest in 1958, which was two years after establishment of the experiment. The pH values (1:1 H₂O suspension) of these plots in order of increasing lime rates were 4.9, 6.0, and 7.1. It is reasonable to assume that the major factor increasing the yield of the orchard grass on the higher lime plots was the increased nitrification rate of those plots.

Nehalem

This experiment was established in the fall of 1958. A good stand of improved species (perennial rye grass-orchard grass-New Zealand white clover) was obtained even on the unlimed plots. Good yields were obtained in 1959. A maximum yield of 9930 pounds per acre was obtained.

There was a significant response to lime within the lime phosphorus factorial, but not within the lime x potassium factorial. The yield increase due to lime amounted to 1500 pounds per acre. About 1400 pounds of this yield increase was obtained with 4 tons of lime per acre. The yield data for the lime x phosphorus and lime x potassium

factorials is given in appendix VII, with the analysis of variance being given in appendix VIII. The yield data given is that calculated from the regression equation. The lack of fit was small and non-significant, which justified the use of the predicted yields. The experimental design used made it possible to calculate a complete 4 x 5 factorial for lime x phosphorus and for lime x potassium from the regression coefficients.

The yield response to potassium, representing 1200 pounds per acre for the 200 pounds per acre was significant in the phosphorus by potassium factorial as was the phosphorus x potassium interaction. Other treatments effects were not significant.

The yield represented very satisfactory forage production for non-irrigated pasture without nitrogen fertilization in this area.

Tillamook

An experiment was initiated on a Tillamook soil the same year as the Nehalem study. However, in this case a fair to poor stand of clover and grass was obtained. Growth during the following spring was so slow that a second cutting was taken from the Nehalem site at the same time of the first cutting on this site.

The 1959 yield data are presented in appendix IX. The yield data presented were calculated from the regression equation as was that for the Nehalem. The lack of fit term for the regression equation was not significant, indicating

that the equation described the actual data satisfactorily. The analysis of variance is presented in appendix X.

Lime produced a yield increase of nearly 1700 pounds per acre, which was significant at the 1 percent level. Other treatment effects were not significant.

Field observations in the spring of 1960 indicated a marked effect of the treatments upon botanical composition. Bent grass (Agrostis species) and june grass (Koeleria crestatata) dominated the plots that had not received lime and phosphorus fertilization. Good stands of rye grass, orchard grass, and clover were present on the plots receiving lime and phosphorus or lime, phosphorus, and potassium treatments.

Yield data for the first harvest in 1960 is presented in appendix IX. Yield increases due to lime, phosphorus, and potassium were significant, while other treatment effects were not (appendix X).

Profile Characterization

One thing in common among the pH values of the soils studied is that they are low. The extremely low values of Clatsop soil, and especially the lower horizons, is considered to be due to the presence of sulfites and sulfides which oxidize to sulfates upon drying (47, p. 100). As a matter of fact, during the acidification step in organic

matter removal for mineralogical studies, the Clatsop samples were adjusted to pH 3.5 with NaOH rather than HCl.

The Nehalem soil, which is derived from recent alluvium, had higher pH values than the other soils. Even so, its highest value was 5.4. The two Ando soils, the Tillamook and Winema, had 1:1 pH values of 4.9 and 4.6 and KCl pH values of 3.9 and 3.7 (table 2).

The determination of soil pH values is traditionally carried out in 1:1 or 1:2 soil:water suspensions. However, it has become rather common in certain European countries, as well as in Japan, to determine soil pH in a 1 N KCl solution. The use of KCl has the advantage of approximating total acidity, whereas, the pH of soil:water suspensions vary with the kind of base saturating cation, amount of salts present, etc. Total acidity would consist of all the hydrogen and aluminum on the exchange complex. A possible liquid junction potential would also be less serious in the KCl suspension.

Russell (47, p. 99) reports that the pH of 1 N KCl soil suspensions is often a whole pH unit lower than the water (soil:water ratio unspecified) pH. It was therefore considered worthwhile to tabulate the difference between the pH values obtained by the two methods (table 2).

For the 0-43 inch depth of the Astoria soil the differences in the pH values for the different horizons was

TABLE 2. pH Values of the Soils Studied as Evaluated by Two Methods

Horizon	Depth	pH		
	Inches	H ₂ O : 1:1	KCl : 1 N	Difference
Astoria Soil				
Ap	0-9	4.7	4.1	0.7
A12	9-23	4.8	4.2	0.6
B11	23-33	4.7	4.2	0.5
B12	43-60 +	4.9	3.9	1.0
Nehalem Soil				
Ap	0-9	5.2	4.1	1.1
C1	9-17	5.0	4.2	0.8
C2	17-36	5.6	4.2	1.4
C3	36+	5.4	4.2	1.2
Tillamook Soil				
Ap	0-7	4.9	3.9	1.0
A12	7-16	4.4	3.9	0.5
A13	17-39	4.7	3.9	0.8
B1	39-50	4.6	4.0	0.6
B2	50-60	4.4	3.9	0.5
Winema Soil				
A11	0-12	4.6	3.7	0.9
A12	12-20	4.6	3.7	0.9
B1	20-31	4.6	3.8	0.9
B2	35+	4.5	3.6	0.9
Clatsop Soil				
Ap	1-6	4.4	3.5	0.9
C1n	8-12	4.1	3.3	0.8
C2H	12-15	3.3	3.1	0.2
C3H	15+	2.9	2.8	0.1

Table 3. Chemical Properties; Organic Matter and Total Nitrogen Content of The Soils Studied

Horizon	Depth Inches	Exchange Cations				C.E.C.	Base Sat.	Organic Matter	Total N	P
		Na	Ca	K	Mg					
		me./100 g.								
Astoria Soil										
Ap	0-9	0.2	0.4	0.2	0.2	24.7	4.2	7.8	0.25	4.2
A12	9-23	0.2	0.4	0.2	0.2	19.4	5.0	5.4	0.18	1.7
B11	23-33	0.1	0.2	0.1	0.2	17.1	4.0	4.4	0.14	2.0
B12	33-43	0.2	0.2	0.1	0.3	17.8	4.4	2.2	0.09	3.0
B2	43-60+	0.2	0.4	0.1	0.8	16.6	8.2	0.8	0.06	1.5
Nehalem Soil										
Ap	0-9	-	24.9	0.8	9.0	55.0	63.0	8.7	0.31	9.8
C1	9-17	0.6	30.2	0.5	8.7	57.5	69.6	6.7	0.30	4.5
C2	17-36	0.5	28.0	0.3	10.4	52.3	75.0	3.8	0.19	6.0
C3	36+	0.6	31.4	0.2	11.3	48.9	89.0	2.4	0.12	8.8
Tillamook Soil										
Ap	0-7	-	2.8	0.6	1.3	54.2	8.7	20.5	0.33	8.0
A12	7-16	0.2	2.0	0.4	1.2	50.6	7.6	16.0	0.64	2.0
A13	17-39	0.4	2.1	0.2	1.0	44.9	8.2	12.5	0.48	1.7
B1	39-50	0.2	0.8	0.2	0.6	39.9	4.8	8.1	0.34	1.5
B2	50-60	0.2	0.4	0.1	0.6	35.4	3.7	2.7	0.16	2.2

Table 3. Continued

Horizon	Depth	Exchange Cations				C.E.C.	Base	Organic	Total	P
	Inches	Na	Ca	K	Mg		Sat.	Matter	N	
		me./100 g.				Percent				PPM
Winema Soil										
A11	0-12	0.2	4.2	1.6	2.8	40.4	21.6	11.2	0.45	5.1
A12	12-20	0.3	1.8	1.1	1.6	36.0	13.4	19.0	0.34	3.6
B1	20-31	0.3	1.1	0.8	1.0	35.4	8.7	6.7	0.28	2.3
B2	35+	0.3	5.1	0.4	0.3	33.4	18.2	2.0	0.12	1.0
Clatsop Soil										
Ap	1-6	1.1	3.7	1.4	4.2	48.7	21.4	16.5	0.52	14.2
Clh	8-12	1.6	2.5	1.1	3.4	39.5	21.8	5.8	0.26	4.5
C2H	12-15	2.2	2.7	1.0	3.8	57.0	17.0	-	-	3.5
C3H	15+	3.8	6.3	1.0	15.9	37.4	72.0	9.2	0.30	3.6

0.6 \pm 0.1 except for the B₂ (43 to 60 inch) horizon, where the difference is 1.0 pH units. For the two Ando soils, the difference varies from 0.5 to 1.0 pH units. It is the Nehalem soil which shows the greatest discrepancy in pH between the two methods while it is in the extremely acid lower horizons of the Clatsop soil that the difference between the two methods is least. It can not be said at this time which method of measuring the soil pH is best, but it is felt that the use of 1 N KCl solution may eventually prove to be more useful. Further study will be required to determine the respective merit of each of the two methods. In the meantime, it is useful to report both the H₂O and the KCl soil suspension pH values.

The exchange capacities of these soils were generally high. The values are in the range of 35 to 55 me./100 g. except for the Astoria soil which had lower values. The Astoria and Tillamook soils had a very low percentage base saturation. These values are comparable with those reported by Kanno (32) for Ando soils. While the status of the Clatsop and Winema soils was intermediate in this regard, Nehalem was very well supplied with exchangeable bases. The exchangeable potassium levels were quite low in the Astoria soil.

The organic matter contents of these soils were generally high in the upper portions of the profile. This

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reflects the abundant vegetative growth, occasioned by the 70 to 90 inch rainfall of this area, in conjunction with dry summers which probably reduce microbiological activity. The Tillamook A_p (1 to 9 inch) horizon had the highest organic matter content (20.5 percent) of any of the samples. The Clatsop and Winema have lesser amounts of organic matter than the Nehalem and Tillamook.

The available phosphorus contents of these soils, based on information obtained on Willamette Valley alluvial soils, were low.

The results of the physical analyses are presented in table 4. The mechanical analyses reveal low sand contents of the Nehalem soil, which is composed primarily of clay and fine silts. Even lower sand contents were found in the Clatsop soil which is composed almost exclusively of fine silt and clay. This was expected in the latter case, as the tideland deposits have been shifted and sorted by wave action which has resulted in these very fine textured deposits. The relatively high sand contents of the Astoria soil may indicate that this soil was derived from sandstone rather than shale. The same would be true for the Winema soil. The difference in sand contents of the Tillamook and Nehalem soils would indicate that the parent material of these two soils was from different sources. In order of increasing fineness of texture, these soils would be ranked

Table 4. Mechanical Analyses, Moisture Retention; Organic Matter and Free Iron Oxide Contents of the Soils Studied

Horizon	Depth	Sand	Coarse Silt	Fine Silt	Clay	Moisture Retention (Percent)		Organic Matter	Free Iron Oxides
	Inches	Percent				5	15	Percent	
Astoria 1									
Ap	0-9	20.8	16.7	30.9	31.2	20.0	19.9	7.8	5.6
A12	9-23	19.8	16.6	31.3	32.2	22.6	18.3	5.4	5.3
B11	23-33	20.2	19.0	28.2	32.4	22.5	15.9	4.4	5.0
B12	33-43	23.1	15.7	26.3	34.9	20.2	17.7	2.2	4.4
B2	43-60+	22.9	12.3	29.0	35.8	20.7	17.7	0.8	5.1
Nehalem									
Ap	0-9	5.1	12.5	48.1	34.4	33.7	24.7	8.7	-
C1	9-17	3.6	9.3	49.3	37.8	33.9	30.5	6.7	6.1
C2	17-36	2.8	7.7	50.0	40.3	32.8	27.9	3.8	6.7
C3	36+	3.7	9.1	49.8	37.4	31.3	26.1	2.4	7.8
Tillamook									
Ap	0-7	13.7	14.8	32.4	39.0	35.7	28.1	20.5	-
A12	7-16	14.9	14.0	32.2	38.9	33.0	29.3	16.0	7.5
A13	17-39	14.0	12.6	32.2	42.5	32.6	26.2	12.5	8.2
B1	39-50	13.8	13.7	33.1	39.4	31.1	24.4	8.1	8.4
B2	50-60	18.8	11.7	32.3	37.2	27.3	23.6	2.7	7.8
Winema									
A11	0-12	21.1	9.9	23.7	45.2	28.1	23.7	11.2	3.8
A12	12-20	20.6	8.3	23.8	47.3	27.2	23.0	19.0	3.6
B1	20-31	19.9	7.2	25.5	47.4	27.0	23.0	6.7	4.0
B2	35+	16.3	8.4	23.6	51.7	25.9	23.4	2.0	4.1
Clatsop									
Ap	1-6	1.4	8.5	49.1	40.9	30.7	25.4	16.5	4.0
C1h	8-12	0.6	2.1	48.2	49.0	31.4	27.2	5.8	2.0
C2H	12-15	-	-	-	-	-	-	-	2.0
C3H	15+	0.5	3.7	52.0	43.9	31.0	27.0	9.2	2.6

as follows: Astoria, Nehalem, Tillamook, Winema, and Clatsop (table 4).

There does not seem to be much variation in the moisture retained between 5 and 15 atmospheres pressure (table 4). The moisture retention at both pressures was generally between 25 and 30 percent except in the case of the Astoria where the values were lower due to its lower clay and organic matter content.

In summarizing the physical properties, then, there were major differences in the size fraction distribution, but smaller differences in the moisture retention values.

Dilute Equilibrium Extracts

One of the purposes of this portion of the study was to obtain a comparison of the release of Ca to equilibrium water extracts by samples from the three field experiments. Since the presence of amorphous inorganic constituents was suspected in these soils, a sample of the Hilo subsoil which is thought to contain a large portion of amorphous materials was included for comparison purposes. The possibility that there might be a relationship between the presence of amorphous materials and the ease of release of Ca to equilibrium water extracts was suggested by the reports of Birrell and Fieldes (6) and Birrell and Gradwell (7). They reported that simply leaching an allophanic clay with water would remove large portions of the exchangeable

bases.

It should be pointed out that in this study a constant cation exchange capacity was used for the different samples rather than a constant sample weight. This approach was used so that differences in the ease of release of Ca and Mg to water extracts would not be confounded with different exchange capacities and, hence, different total amounts of Ca+Mg present in the different soils at given percent Ca+Mg saturation. Another advantage was that the results of these Ca release studies could then be compared with those of Chao (13) for reference minerals.

The soil samples used in this portion of the study were taken from the three field experimental sites. The differing degrees of Ca+Mg saturation reflect the different rates of lime applied to the particular plots. In the case of the Hilo subsoil, different degrees of Ca+Mg saturation were obtained by adding varying amounts of $\text{Ca}(\text{OH})_2$.

The curves in figure 1 show the relationships between the pH of equilibrium extracts and the percent Ca+Mg saturation, while figure 2 shows the relationships of the concentration of Ca+Mg in equilibrium extracts to percent Ca+Mg saturation.

Because of the limited number of points available, not all of the inflections of the curves are clearly defined. Where there appears to be a reasonable question as to the

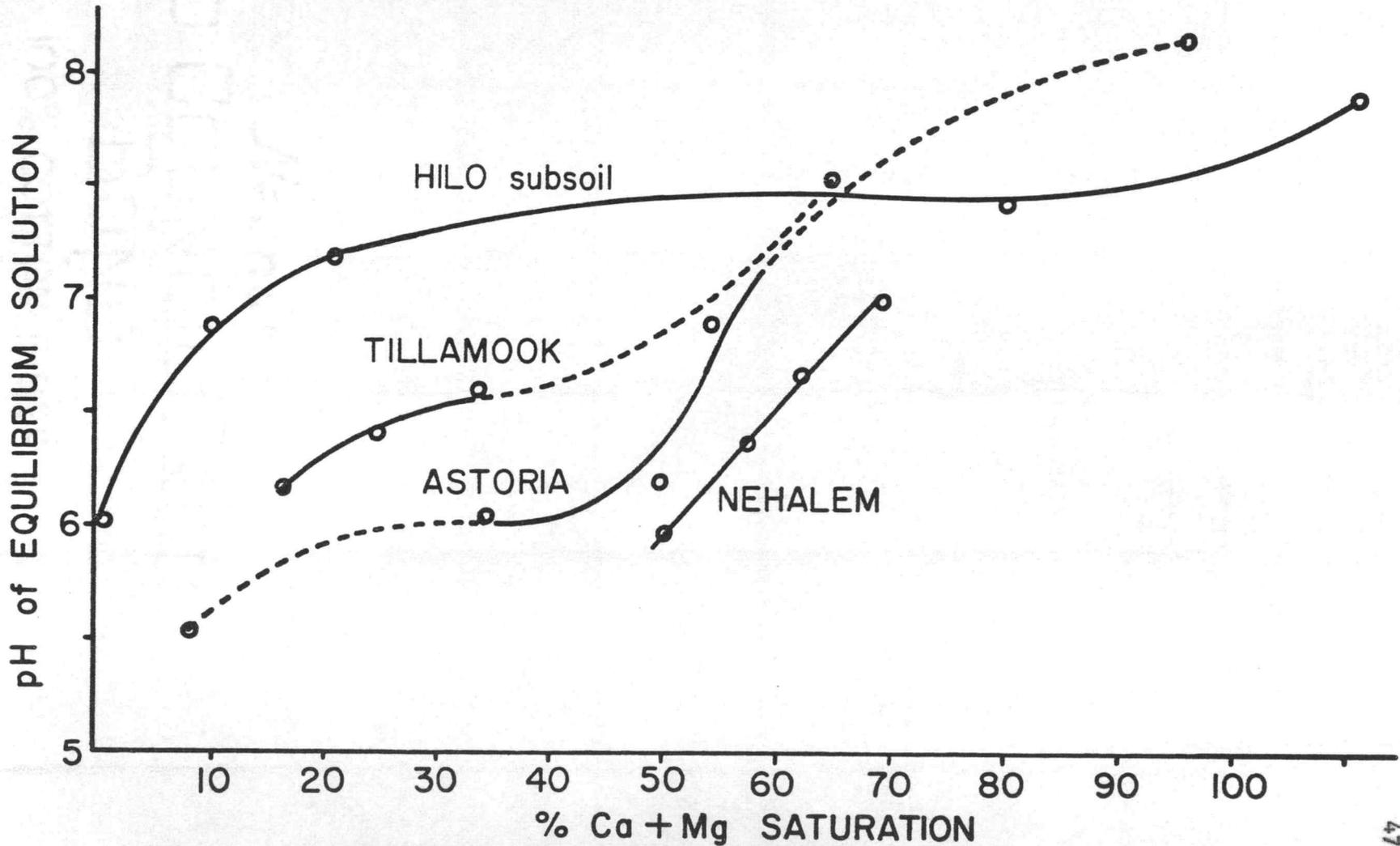


Figure 1. pH of Equilibrated Water Extracts Versus Percent Ca+Mg Saturation of the Exchange Complex

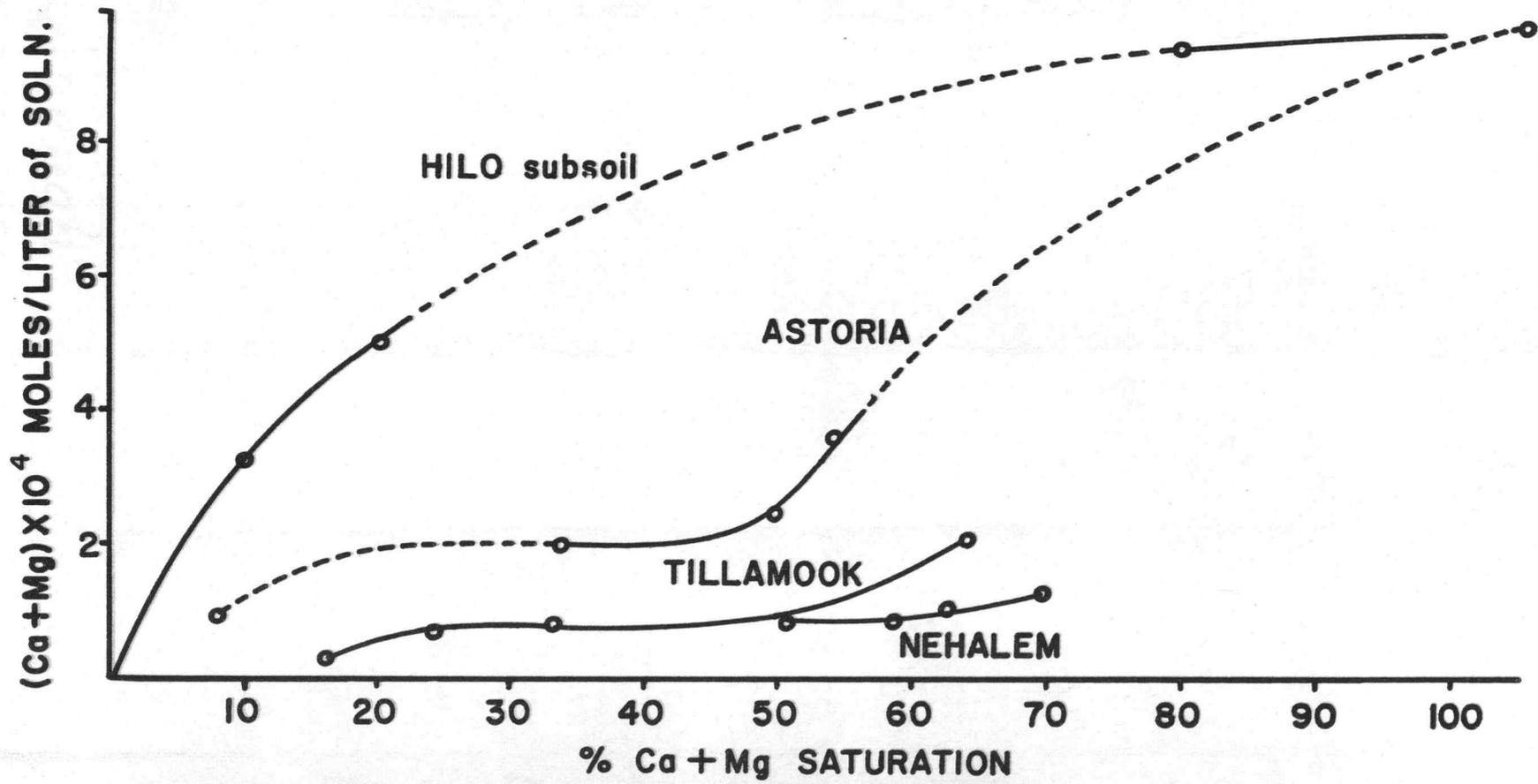


Figure 2. Ca+Mg Concentration in Dilute Equilibrated Water Extracts Versus Percent Ca+Mg Saturation of the Exchange Complex

shape of the curve a dashed rather than solid line was drawn. This problem occurs with the Astoria soil and the Hilo subsoil.

Tillamook soil, and the Astoria as well if the curve is drawn correctly, is predominately aluminum rather than hydrogen saturated. This is inferred by comparison of the inflection in the initial portion of the curve of the titration curves with those of Chao (14) for reference minerals. Chao found that for hydrogen saturated bentonite, illite, and kaolinite the first inflection point on the pH of equilibrium solution versus Ca^+Mg saturation curve occurred at Ca saturations of greater than 40 percent. An initial inflection point occurred below 20 percent for the same minerals when aluminum saturated.

The shape of the Ca^+Mg release curves for the Astoria and Tillamook are quite similar though the Astoria releases roughly twice as much Ca^+Mg to the equilibrium solution at a given Ca^+Mg saturation than does the Tillamook soil. The Nehalem soil shows only a very slight increase in Ca release with an increase in Ca^+Mg saturation from 50 to 70 percent. In this same range of percent Ca^+Mg saturation, the amount of Ca^+Mg released by the Astoria soil is more than doubled. The same is probably true for the Tillamook soil.

The Hilo subsoil is well buffered between pH 7.2 and

7.4. This increase in 0.2 pH unit represents an increase in Ca+Mg saturation of 60 percent.

The Ca release curve of the Hilo subsoil substantiates the reports (6, 7) of the ease with which amorphous materials release exchangeable cations. The Ca release curve of the Hilo subsoil appears to bear little relation to the Ca release curves of the soils.

The concentration of potassium in equilibrium extracts was also determined. In general there was an increase in the concentration of potassium in equilibrium extracts with increasing percentages of potassium saturation. The data are presented in appendix IV.

Mineralogy

Free Iron Oxides

Free iron oxides is a somewhat ambiguous term, and it may be well to consider first what it means. Mackenzie (37) defined free iron oxides as "all iron not present in the crystal lattice of any component mineral, excepting, of course, the iron oxide minerals themselves". Since he presented no data showing that the iron oxide minerals were actually dissolved, the results of other studies of iron oxide removal were considered. The free iron oxide removal studies reviewed here all used a common reducing agent, namely, $\text{Na}_2\text{S}_2\text{O}_4$.

Mehra and Jackson (42) found that finely ground hematite and goethite were essentially completely dissolved (98 to 100 percent). Stace (48) had previously shown that hematite smaller than 70 mesh would be almost totally dissolved by free iron removal treatments. Stace also found that an ilmenite containing 89 percent Fe_2O_3 released iron calculated as 11.7 percent Fe_2O_3 of the sample and a biotite containing 28 percent iron as Fe_2O_3 released iron equivalent to 2.3 percent Fe_2O_3 . However, since a single extraction was reported, it is not known to what extent the iron released from these two minerals represents iron oxide impurities and to what extent it reflects the decomposition of layer silicates. Mehra and Jackson (42) have shown that decomposition of some layer silicates and clays is relatively small as evidenced by change in cation exchange capacity. Vermiculite and a Bayamon clay sample were not affected. The exchange capacity of nontronite and allophane were somewhat decreased. Although no information relative to the resistance of magnetite to these treatments was found, it is probably not attacked.

The two methods in common use are those of Jackson (28, p. 57) and Mackenzie (37). The method of Jackson was chosen for use in this study because it was considered to have the following advantages: 1) since citrate is used to complex the iron as it is reduced, the acid used to

dissolve precipitated iron sulfides in the Mackenzie method is unnecessary and the question of whether or not all the sulfides were dissolved does not arise; 2) since the acid wash is unnecessary, the number of digestions and centrifugings are cut in half; 3) the uncertain effect of dilute acid (0.05 N) on soils containing amorphous aluminosilicates is avoided; 4) the system is buffered at pH 7.3 which has since been shown to give maximum iron oxide removal (42); 5) the $\text{Na}_2\text{S}_2\text{O}_4$ is added directly to the soil suspension (Jackson method) rather than adding it as a solution (Mackenzie method), since this salt immediately begins to decompose in water and there is some loss in effectiveness as well as production of unpleasant odors; and 6) the number of iron determinations is less by one-half as the $\text{Na}_2\text{S}_2\text{O}_4$ and HCl extracts must be kept separate in the Mackenzie method.

The iron removed from these profile samples, expressed as Fe_2O_3 , was computed on the basis of the oven dry, organic matter-free sample weight and are given in table 4. By calculating the results in this manner rather than on an oven dry basis, the comparisons are more meaningful.

The Tillamook soil has the highest free iron oxide content of any of these five soils. In order of decreasing quantities present were Nehalem, Astoria, Winema, and Clatsop soils. The two Ando soils differed considerably

in their free iron oxide contents, the values for the Tillamook being twice as high as those of the Winema. The values of the 8 to 12 and 12 to 15 inch depths of the Clatsop soil are quite low.

The free iron oxide contents show a minimum of differences between horizons. With the exception of the Astoria B₂ (43 to 62 inches), no zones of accumulation were evident (table 4). The free iron oxide content of the Nehalem soil increases with depth. Since this is a relatively young soil that still has a base saturation of 65 percent, this increase of iron oxide content with depth is thought to represent differences in the free iron oxide content of the parent material. The Tillamook soil has slightly higher values in the A₁₃ (17 to 39 inches) and B₁ (39 to 50 inches) horizons. The Winema shows little difference in free iron oxide content of the various horizons.

X-ray Diffraction of Sand and Silt Fractions

A variety of information is obtainable from studies of the mineralogy of sand and silt fractions of soils. Some inferences may be drawn as to the potential nutrient supplying power of soils if the minerals present in their sand and silt fraction are known. Information regarding the degree of weathering and the relative age of soils has also been obtained from mineralogical studies of sand and silt fractions. The source of parent material of alluvial soils

has sometimes been identified by the minerals, or rock fragments, present in them. Of the various possible techniques for obtaining mineralogical information on these fractions, X-ray diffraction was chosen.

In the majority of the cases, minerals found in one of the sand or silt fractions was present in the other two as well. Only minor mineralogical differences among these size fractions were found between horizons of a given soil. Additionally, only minor differences were found between soils with regard to the occurrence of quartz and feldspars. Quartz was found in all of the samples studied. Indeed, it would have been surprising if quartz had not been found in all the sand and silt fractions of these soils. This is because silt and sand sized quartz is essentially resistant to weathering.

Feldspars as a group are easy to identify as they all have their most intense reflection between 3.10 to 3.30 Å (27 and 28° 2θ), while the majority have their most intense reflection within the relatively narrow range of 3.18 and 3.24 Å. Based on the presence of a peak between 3.18 and 3.24 Å, feldspars were identified in all but one or two of the sand and silt fractions examined. The feldspar peak intensities tended to be a little greater in the Nehalem than in the other soils.

Detailed examination of the patterns revealed a feldspar doublet occurred in the patterns of Astoria, Tillamook,

and Winema soils but not of the Clatsop or Nehalem soils. In the samples showing the doublet, the low angle peak varied from a d value of 3.26 to 3.24 Å with a mean of 3.25 Å while the high angle peaks (lower d values) varied from 3.22 to 3.20 Å with a mean of 3.21 Å. Only the high angle peak component occurred in the Nehalem and Clatsop patterns.

Because of the obvious relation of potassic feldspars to the potential potassium fertility of soils, it would be useful if the individual feldspars present in these soils could be identified. A brief search of the literature was made to see what success others had experienced in identifying the individual feldspars by X-ray diffraction.

Phillippe and White (45), who studied quantitatively the presence of the three feldspars, microcline, albite, and orthoclase, used reflections at 3.24 Å for microcline, 3.20 Å for albite, and 3.29 Å for orthoclase. However, in a subsequent paper, Caldwell and White (11) make the following comment,

"However, it was found that determination of percent feldspar in the soil samples on the basis of allocation of area between the microcline (3.24 Å) and albite (3.20 Å) peaks, was not feasible under the conditions of this experiment."

Instead, they used the combined area of the feldspar peaks from 3.13 to 3.28 Å, which was the area enclosed by extrapolation of the slopes of the feldspar peaks to the background line.

Based on the work of Phillippe and White (45), Johnson and Beavers (31) also used the 3.24 Å line for identifying microcline and the 3.20 Å line for albite.

In a study of marine sediments, Zen (58) considered that the 3.18 Å ("at about 28°20") line was due to plagioclase feldspars which "commonly, though not invariably, shows multiple peaks". He mentioned that the multiplicity of peaks could possibly be due either to the presence of anorthite in excess of about 30 percent by weight or to plagioclase grains of different composition and hence different lattice spacings. The presence of a plagioclase was confirmed by optical methods. Because the grains commonly gave at least one index of refraction greater than 1.56, the plagioclase was thought to be rather calcic. In the same study, potassic feldspar was identified by a 3.24 Å (at 27.5° 20) reflection, but was not observable under the microscope.

Theisen (personal communication) has identified albite, labradorite, and oligoclase in the fine silt of an eolian deposit by X-ray diffraction. In contrast to the previous authors, Theisen based his identification upon the presence of a number of reflections (hkl) of a given feldspar mineral.

To verify the validity of the d values used by the

authors noted above for identification of specific feldspars, reference was made to the American Society for Testing Materials X-ray Index (8). The three most intense lines of the feldspar patterns therein listed are given in table 5. It is evident that, contrary to what might be expected, there is little or no grouping of the feldspars into the potassic series (sanidine ^{13/}, orthoclase, and microcline), the plagioclase (sodium-calcium) series (albite, oligoclase, andesine ^{13/}, laboradorite, bytownite, and anorthite), or the potassium-sodium series (sanidine or orthoclase, anorthoclase ^{13/}, and albite) according to the location of their most intense reflection. Further, there is a minimum of similarity between different patterns of the same mineral when considering the 3 most intense lines. For example, albite is variously reported to have its most intense reflection at 3.19, 3.20, 3.21, and 3.30 Å (see numbers 3-0508, 1-0709, 2-0515, and 3-0451) while the second and third most intense reflections show even more variation in d values. The most intense reflection of microcline is given as 3.24 and 3.26 Å (numbers 2-0513 and 3-0471) which brackets by 0.02 Å the value used by Phillippe and White (45). There would thus appear to be a very high degree of uncertainty in assigning the 3.20 Å reflection to albite since there seems to be no reason why this reflection

^{13/} No patterns are given for sanidine, andesine, or anorthoclase.

Table 5. d Values and Relative Intensities of the Three Most Intense Lines of Feldspars as Listed in the ASTM X-ray Index

ASTM NO.	Feldspar	d Value (Relative Intensity)		
3-0559	Anorthite	3.10 (100)	2.45 (50)	2.08 (30)
2-0532	Oligoclase	3.18 (100)	4.07 (80)	3.67 (80)
2-0534	Orthoclase	3.18 (100)	4.02 (80)	3.80 (80)
4-0571	Bytownite	3.18 (100)	4.02 (50)	2.50 (40)
3-0505	Anorthite	3.19 (100)	2.51 (70)	4.04 (60)
3-0508	Albite	3.19 (100)	1.79 (60)	3.97 (50)
1-0739	Albite	3.20 (100)	4.05 (35)	3.66 (25)
2-0509	Labradorite	3.22 (100)	2.53 (50)	1.82 (50)
3-0499	Labradorite	3.20 (100)	4.07 (40)	2.53 (27)
2-0523	Anorthite	3.20 (100)	2.51 (50)	2.14 (50)
2-0537	Anorthite	3.18 (100)	2.51 (50)	4.03 (30)
2-0515	Albite	3.21 (100)	4.11 (50)	2.95 (50)
2-0513	Microcline	3.22 (100)	1.80 (80)	2.16 (70)
3-0471	Microcline	3.26 (100)	4.25 (38)	2.16 (25)
2-0475	Orthoclase	3.29 (100)	1.81 (90)	4.25 (70)
3-0451	Albite	3.30 (100)	4.20 (60)	3.86 (60)

could not be indicative of labradorite or anorthite as well. Whiteside (57) also noted this problem when establishing the quantities of feldspars present in loessial soils. He reported that,

"Since the 3.20 Å diffraction line of albite is more intense than that of the diffraction line of some of the plagioclases, orthoclase, or microcline, the tabulated estimates are actually minimum values. These estimates could be too low by as much as 35% of the feldspar content if the feldspar present was actually microcline."

Since the different feldspar specimens differ so greatly in the relative intensities of the different reflections, it would appear that it is not possible to identify a given feldspar on the basis of a single reflection, as has been reported. It is probably necessary to use optical means to identify the specific feldspar minerals present.

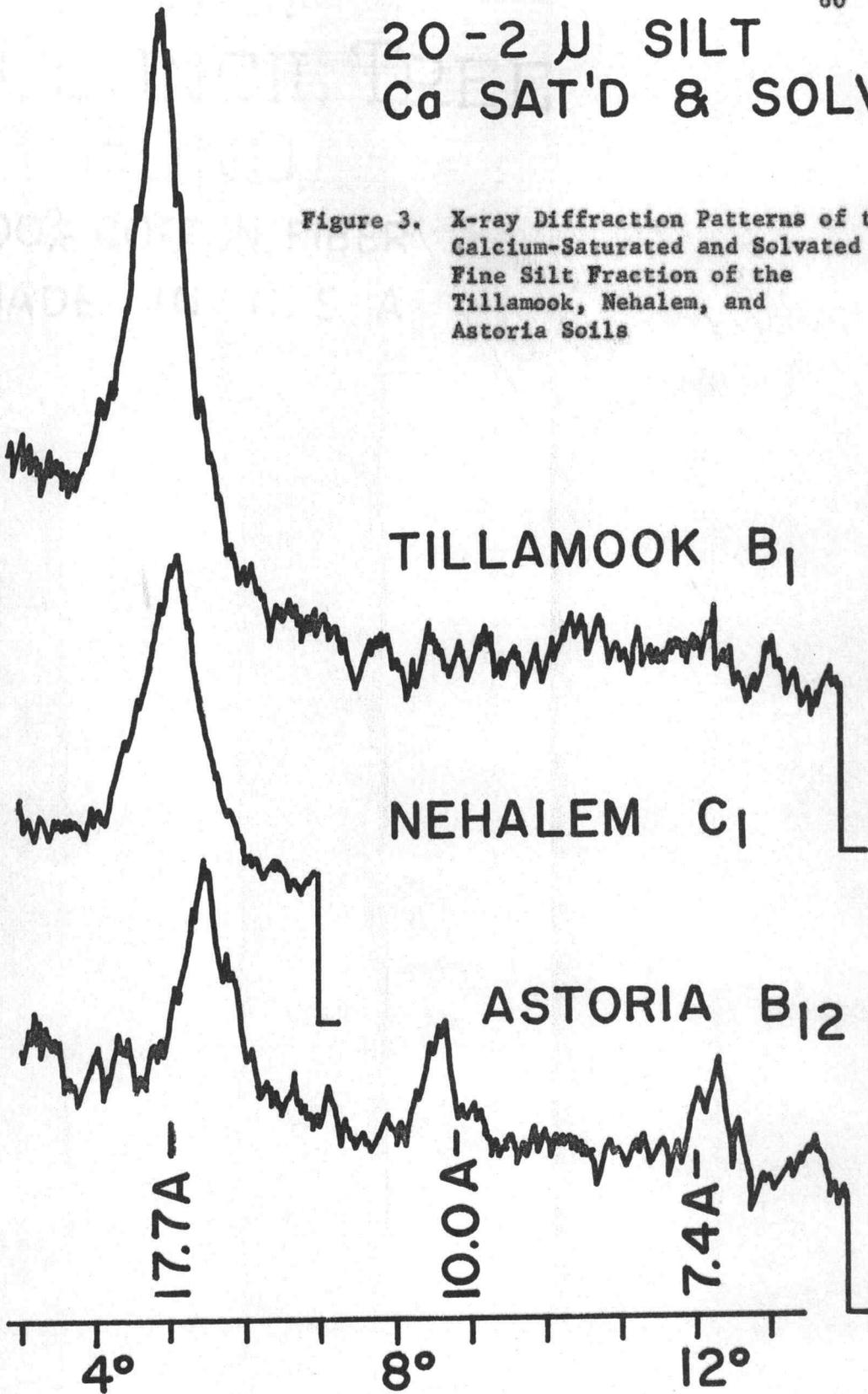
Having discussed the occurrence of primary minerals, we will now consider the secondary minerals found in sand and silt size fractions. These results can best be presented on a soil by soil basis. Some representative patterns of the silt fractions are presented in figure 3.

Illite^{14/} was found to occur in the Astoria soil in both the sand and silt size fractions while montmorillonite and kaolinite occurred only in the silt fractions. A suite

^{14/} The name illite is used in the sense of Grim (23, p. 35) and applies to all layer silicates giving a 10 Å reflection (which would include muscovite, biotite, or glauconite).

20-2 μ SILT Ca SAT'D & SOLV.

Figure 3. X-ray Diffraction Patterns of the Calcium-Saturated and Solvated Fine Silt Fraction of the Tillamook, Nehalem, and Astoria Soils



of layer silicates similar to that of the Astoria was found in the Tillamook and Winema soils. However, in the case of these two soils, montmorillonite and kaolinite were sometimes found in the sand fraction.

In the Clatsop soil, kaolinite and illite were identified in the silt fractions only.

In the Nehalem soil only montmorillonite was identified in the silts.

In view of the large quantities of montmorillonite present in the 2 to 0.2 micron fraction of these soils (discussed in a later section), it is not surprising that some clay size montmorillonite would remain in the fine silt in spite of repeated washings (5 or 6) during fractionation. Brief observations under the petrographic microscope of one sample (Nehalem, 17 to 36 inches depth) have indicated the additional possibility that clay aggregates may be present in the fine silt in spite of the rigorous dispersion technique used. In this connection, the findings of McAleese and Mitchell (40) that montmorillonite as well as vermiculite occurs as true silt size particles are of interest. It is not completely clear why, in the silt fraction of the Clatsop, the clay separation was more effective and no montmorillonite was detected in the silt fraction. The suggestion of Grim, et al. (25) that the presence of considerable sodium tends to keep montmorillonite highly

dispersed in very recent sediments may have merit in the Clatsop soil. The exchangeable sodium of this soil increases from a value of 1.1 for the 1 to 6 inch depth to 3.8 me./100 g. at the 15 inch depth (table 3).

X-ray Diffraction of Clay Size Fractions

Diffraction analyses of parallel-oriented specimens were run on the 3 clay size fractions. Duplicate calcium- and potassium-saturated specimens and a single solvated calcium specimen were run in all cases. Heat treatments were applied as needed. The results of this study are discussed for each soil on a profile basis.

The only layer silicate that could be identified in the Nehalem soil was montmorillonite. This was true for all clay size fractions and all horizons. This would indicate the probability of a uniform source of the parent material of this soil. It would leave unexplained the results of Cattani (12) who found a much higher NH_3 fixation in the C_3 horizon of this soil than in the remainder of the profile.

The clay mineralogy of the Winema differed from that of the Nehalem in that kaolinite was found to occur in the coarse clay (2 to 0.2 micron) fraction throughout the Winema profile. There was also a slight indication of kaolinite in the medium clay fraction of the upper portion of

the horizon. Based on relative peak intensities there appeared to be more kaolinite, relative to montmorillonite, in the lowest horizon sample than in the upper ones. There is also some evidence of interstratification as evidenced by the asymmetry of the montmorillonite peak. A portion of the 14 Å expanding component also appears to be an intergrade as evidenced by only partial collapse of the 14 Å peak to 10 Å upon heating to 300° C.

Montmorillonite was also found to be the dominant layer silicate in the Tillamook, though this soil also contained a quantity of kaolinite which occurred primarily in the coarse clay with lesser amounts in the medium clay. There were occasional very weak 10 Å reflections in either the 2 to 0.2 or the 0.2 to 0.08 micron fractions, suggesting the presence of some illite.

In the Clatsop, a tideland soil, the peak intensities of the coarse clay fraction of illite and kaolinite were about one-third the intensity of the montmorillonite peak. Traces of kaolinite, but not illite, occurred in the medium clay fraction.

Of these five soils only the Astoria offered a challenge in the interpretation of the X-ray diffraction patterns of the parallel orientation specimens (figure 5). Calcium-saturated slides revealed the presence of 7, 10, and 14 Å peaks. The 14 Å clay reflections of the coarse

Ca SATN. & SOLV.
2-0.2 μ

Figure 4. X-ray Diffraction Patterns of the Calcium-Saturated and Solvated Coarse Clay Fraction of the A₁ Horizon of the Nehalem, Clatsop, Tillamook, and Winema Soils

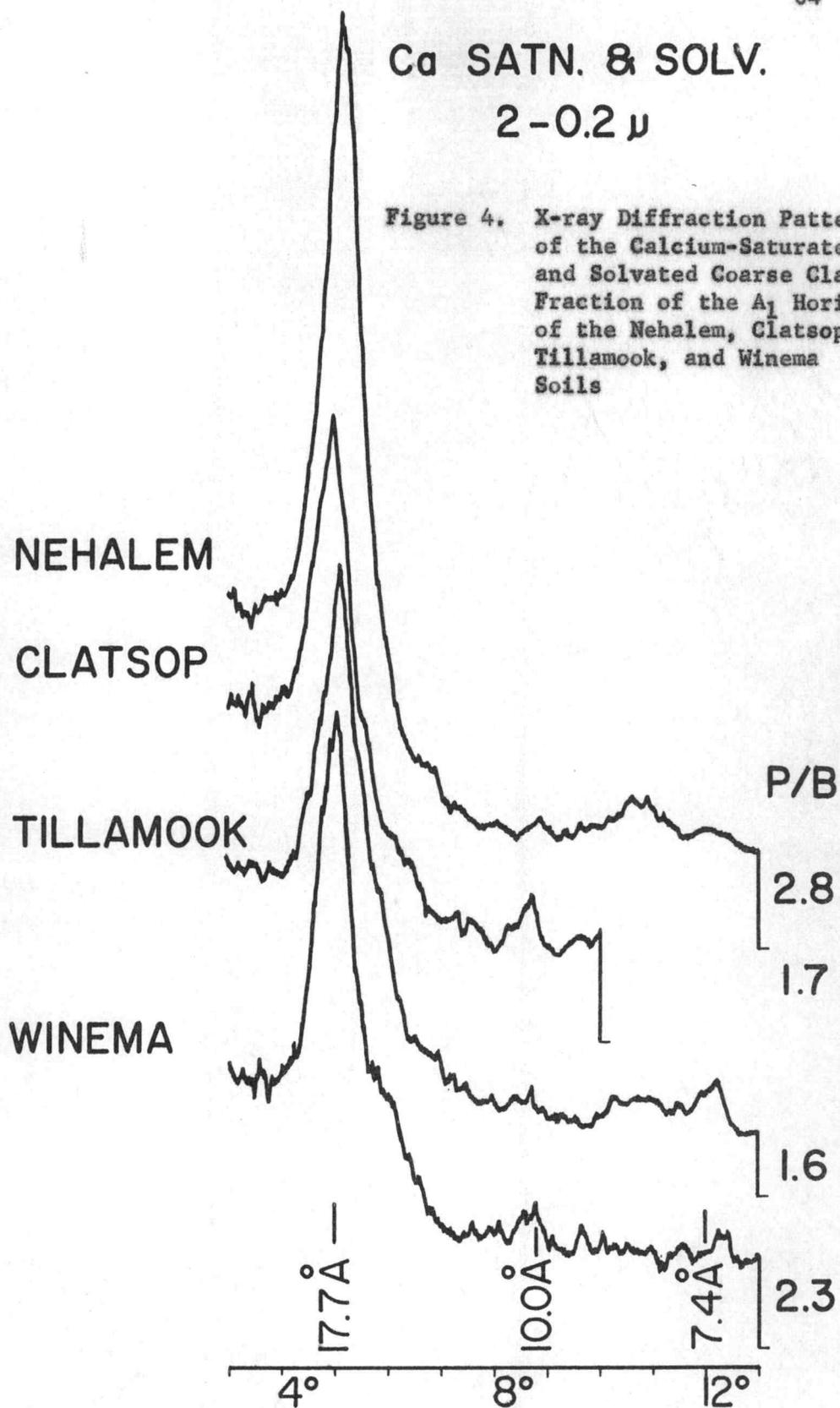
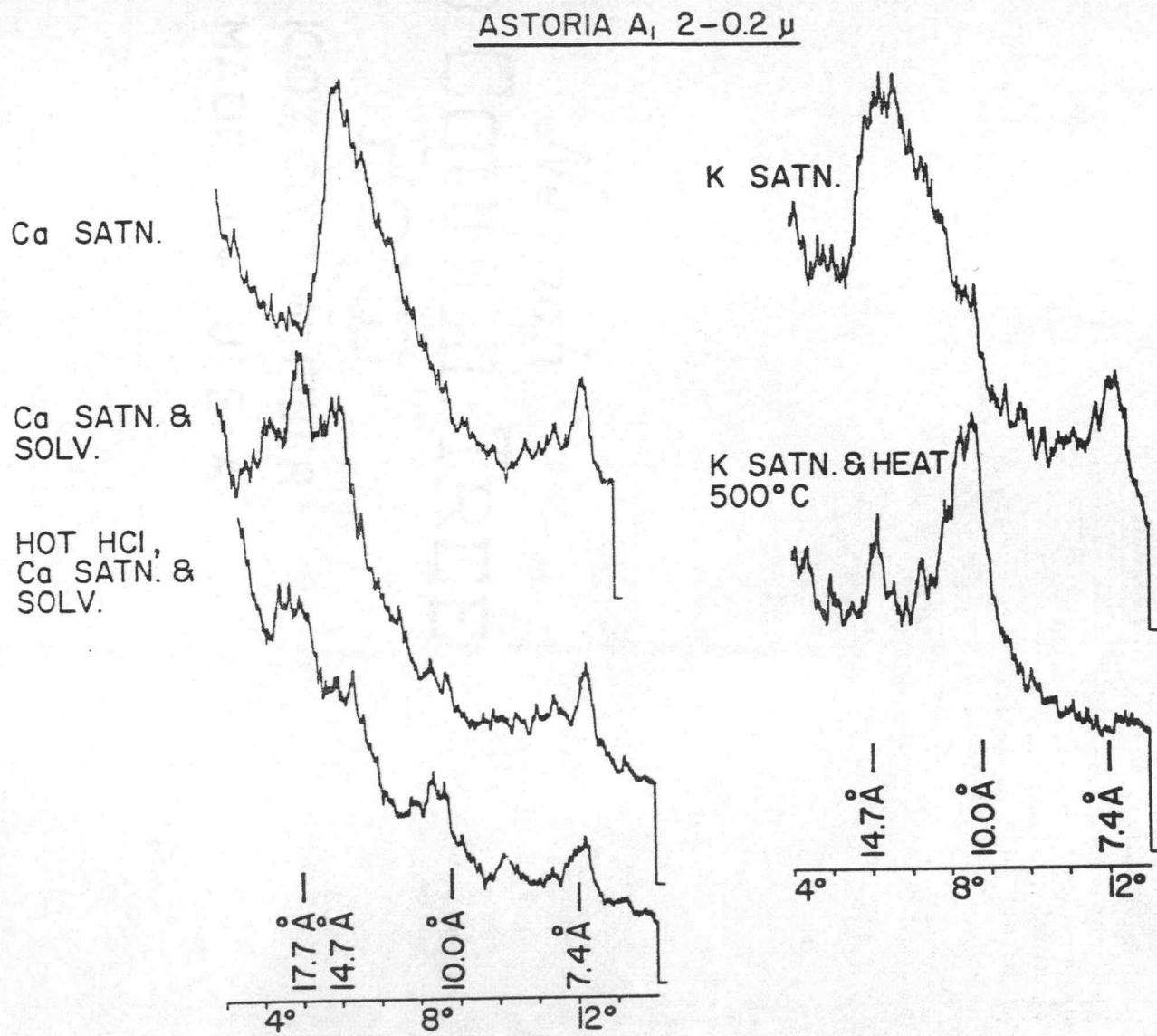


Figure 5. X-ray Diffraction Patterns of the Coarse Clay Fraction of the Astoria A₁ Horizon



clay fraction were asymmetric, with the high angle side having roughly a constant slope from background to the peak. Both the broadness and the asymmetry of the 14 Å peak indicate interstratified montmorillonite-illite (58).

Solvation of the calcium-saturated specimen revealed the presence of montmorillonite and a non-expanding component in the coarse clay fraction. The non-expanding component was absent from the medium or fine clay fraction. The non-expanding component in the solvated pattern of the coarse clay could have been either vermiculite and/or chlorite. Therefore, a potassium-saturated specimen was heated to 500°C. to determine if chlorite were present. Examination of the diffraction pattern after this treatment revealed that while part of the 14 Å peak had collapsed to approximately 10 Å, a 14 Å component remained, indicating that chlorite was present. On the basis of these treatments, it was not possible to determine whether vermiculite was also present or not.

The presence of chlorite makes the identification of kaolinite by X-ray diffraction very difficult. This is because the second order of chlorite coincides with the first order of kaolinite. The 7 Å kaolinite and chlorite reflections are both eliminated by heating to 500°C. It was thought that if the chlorite could be dissolved, it might then be possible to determine if kaolinite and/or

vermiculite were present.

Duplicate calcium- and potassium-saturated specimens were prepared from the 2 to 0.2 micron fraction of the Astoria A₁, according to the hot HCl method of Brindley and Youell (9), as described under methods. Without the hot HCl treatment, the 14 Å peak of the calcium-saturated specimens was asymmetrical to an extent that the high angle side overlapped the 10 Å reflection. After the HCl treatment, there was a sharp 10 Å line and a broad 14 Å line. Potassium-saturation accentuated the intensity of the 10 Å peak while solvation reduced its intensity, and gave a relatively small 17 and a 14 Å peak having about 80 percent of its former intensity. It is not known if the small remaining 14 Å peak is undissolved chlorite or vermiculite, although it seems most probable that it is the latter. The HCl treatment appeared to have caused a marked reduction in the intensity of the montmorillonite peak. Presumably this was caused by dissolution of the montmorillonite as well as chlorite. The asymmetry of the calcium-saturated Astoria coarse clay would indicate random interstratification of montmorillonite and illite with the former being the dominant member. The considerable increase in intensity of the 10 Å line of the calcium-saturated specimens, as a result of the HCl treatment, is of interest. If there were vermiculite or montmorillonite present as impurities, they should

expand to 14 Å with calcium saturation. Therefore, it may be that the 10 Å spacing results from the removal of the brucite layer from the chlorite. It is not clear why the C-axis spacing remains at 10 Å upon calcium saturation instead of expanding to 14 Å as would montmorillonite and vermiculite. This is apparently a direct result of the HCl treatment as Gardner (20) found that a 10 Å line appeared on calcium saturated prochlorite after leaching with 0.1 N HCl.

The 7 Å peak was reduced by 10 to 30 percent, on duplicate calcium-saturated specimens, as a result of the HCl treatment. This would indicate that approximately 80 percent of the former intensity 7 Å peak in prior calcium saturated specimens was due to kaolinite.

To substantiate the data just presented for the presence of kaolinite, the method of Johns, Grim, and Bradley (30) was applied to potassium saturated slides of the A₁₂, B₁₁, and the B₁₂ horizons. This involves heating the slide gradually to 450°C. in 45 minutes, then quenching in air. These authors found that at 450°C. no kaolinite that they examined had lost its 7.2 Å reflection by this heat treatment, but quite a number of the chlorites did. When the coarse clay of 3 horizons were thus treated, there was a decrease in the intensity of the 7.2 Å reflection to approximately 80 percent of its former value for the A₁₂ and

to 70 percent of the former values for the B₁₁ and B₁₂ horizons. Thus, based on the method of Johns, Grim, and Bradley (30), about 3/4 of the intensity 7.2 Å reflection of this profile would appear to be kaolinite.

It was observed in the patterns of the fine clay fraction (figure 6) that in going from the A₁ to the B₂ horizon the 17 Å (solvated) montmorillonite peak gradually fades into the apparent background. The intensity, calculated as counts per second (average of duplicate calcium saturated slides) above the apparent background, decreases as follows, 80, 52, 10, 0, 0 for the A_{1P}, A₁₂, B₁₁, B₁₂, and B₂ horizons respectively. This situation suggests the presence of amorphous aluminosilicates, whose presence increases the background and interferes with preferred orientation, and a corresponding decrease in crystallinity. This increase in the apparent background is also caused in part by extensive interstratification of the fine clay fraction.

In summary, then, montmorillonite, chlorite, illite, and kaolinite have been found in the coarse clay fraction of the Astoria soil with some kaolinite and/or chlorite in addition to montmorillonite in the medium clay fraction, while only montmorillonite occurred in the fine clay. The presence or absence of vermiculite was not established.

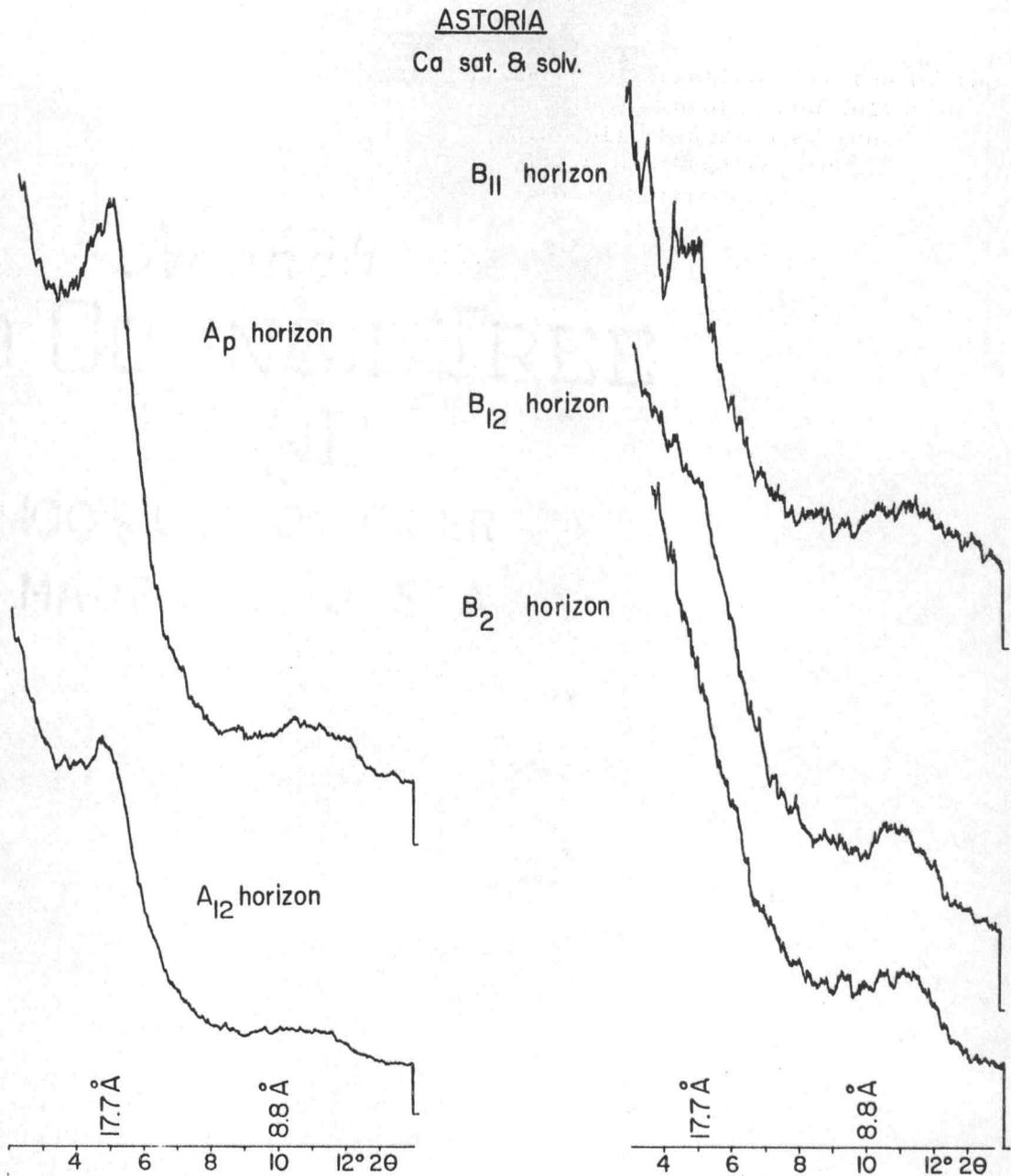


Figure 6. X-ray Diffraction Patterns of Calcium-Saturated and Solvated Fine Clay Fractions of the Astoria Profile

Cation Exchange Capacity Delta Value

X-ray diffraction studies of the fine clay fractions of these soils had indicated the probable presence of amorphous material in the Astoria soil. The morphological similarities of the Tillamook and Winema soils to the Ando soils of Japan raised the question of whether they were similar mineralogically. This is of interest since amorphous material is the chief constituent of the clay fraction of the Japanese Ando soils (3). Therefore, the method of Aomine and Jackson (2) for identifying "allophane of the type occurring in the Ando soils" appeared to be particularly promising.

The phenomenon which causes a large differential in the cation exchange capacity, depending upon whether the sample is pretreated with an acid or a base, is apparently a unique property of allophane (2).

Aomine and Jackson (2), analyzing two geological specimens, found delta values of 82.7 and 110.8 me./100 g. Of 6 clays (less than 0.2 microns) from Japanese soils derived from volcanic ash, the highest delta value obtained (soil number 22, containing only a slight amount of vermiculite as an impurity) was 101.6 me./100 g. Since this was in the range of the values for the geological specimens and the sample was relatively pure, they averaged it in with the 2 geological specimens to come up with a value of 98.4.

They then took the figure of 100 me./100 g. as the "first approximation for standard delta value for Ando type allophane determination". These authors also reported values for single samples of montmorillonite, kaolinite, gibbsite, and quartz as listed in table 6.

Since the reported values for the layer silicates were for single samples and no delta values were available for some of the layer silicates occurring in the soils studied here, it seemed necessary to study some reference minerals. The delta values determined for reference minerals are given in table 7. The difference in the delta value for the montmorillonite given here and that in table 6 is rather striking, differing by a factor of 100. Where Aomine and Jackson found the delta value of kaolinite to be zero, a value of 6.7 was found here. Other delta values determined for reference minerals are as follows: 7.5 for illite; 2.8 for vermiculite; and 1.7 for prochlorite.

A sample of Japanese allophanic clay gave a value of 75.3 while a Hilo subsoil sample gave a value of only 14.1. It is suspected that the delta value for the Hilo subsoil would have been much higher had the sample not been dried previous to determining the delta value. The soils in Hawaii which are high in amorphous materials are known to dry irreversibly while the Ando soils of Japan do not. It is thought that the fact that the Hawaiian soils dry

Table 6. Cation Exchange Delta Value of Several Standard Materials, Oven Dry Basis; After Aomine and Jackson (2)

Mineral	Treatment		Delta Value
	Acidic	Basic	
	me./100 g.		
Allophane (Choyo)	55.6	157.2	101.6
Allophane (white)	60.6	143.3	82.7
Allophane (brown)	44.1	154.9	110.8
Halloysite (Indianite)	12.3	30.2	17.9
Montmorillonite, Wyo.	77.9	88.0	10.1
Kaolinite, S. C.	4.6	4.6	0
Gibbsite	2.6	3.1	0.5
Quartz	0.0	0.0	0

Table 7. Cation Exchange Delta Value and Sodium Hydroxide Solubility of Some Reference Minerals

Mineral		Treatment		Delta Value	Percent Weight Loss	
		Acidic	Basic		(accumulative)	
		me./100 g.			First	Second
Montmorillonite	24	89.4	89.5	0.1	7	7
Kaolinite	4	1.8	8.5	6.7	3	-
Illite	35	2.5	10.0	7.5	3	-
Vermiculite		8.4	11.2	2.8	-	-
Prochlorite	6	1.8	3.5	1.7	5	-
Allophane (Japan)		2.7	78.0	75.3	58	64
Allophane (Hilo subsoil)		1.3	15.4	14.1	70	67

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irreversibly indicates that the cation exchange delta value would be decreased by drying. Oven dry samples were used as this is part of the procedure of Aomine and Jackson (2).

It is to be regretted that Aomine and Jackson (2) did not determine delta values on a series of montmorillonites and halloysites, as well as illites and kaolinites. The variation in the values given here and those reported by Aomine and Jackson would raise a question as to the validity of calculating the quantity of allophane based upon an allocation of the delta value to the various mineral components.

Visiting soil scientists who have had experience with soils containing appreciable amounts of amorphous aluminosilicates had commented on its probable presence in the Astoria soil. It was therefore interesting to find a low delta value for the 0 to 9 and 9 to 23 inch depths (table 8). However, the value of 14.1 at the 33 to 43 inch depth would indicate that appreciable allophane is present at this depth. The second unexpected result was the relatively high values for the Nehalem soil, 20.5 and 25.6 for the 0 to 9 and 9 to 17 inch depth respectively. This soil, from recent alluvium with an A-C profile, is a relatively young soil with a minimum of profile development. It is, therefore, concluded that a major portion of the allophane of this soil was inherited rather than having formed in place.

Table 8. Cation Exchange Delta Values and Sodium Hydroxide Solubility of Selected Profile Samples

Soil	: Depth :	Pretreatment		Delta Value	Weight Loss
		Acidic	Basic		
		: Inches :	me./100 g.		
Astoria	0-9	1.9	10.7	8.8	8
Astoria	9-23	2.0	9.3	7.3	16
Astoria	33-43	16.6	30.7	14.1	15
Nehalem	0-9	40.3	60.7	20.5	12
Nehalem	9-17	53.7	79.3	25.6	12
Tillamook	0-7	26.6	43.9	17.3	23
Tillamook	7-16	35.0	54.4	19.3	--
Tillamook	39-50	--	--	--	25
Winema	0-12	18.5	35.5	17.0	8
Winema	12-20	20.5	36.8	16.3	14
Clatsop	1-6	19.6	38.1	18.5	10
Clatsop	8-12	26.6	47.1	20.5	22

The lower delta value of the surface horizon relative to that of the 9 to 17 inch depth might be taken to indicate that the quantity of allophane in the 0 to 9 inch depth is decreasing. Another possibility is that these two horizons represent different source areas. However, X-ray diffraction as well as chemical properties failed to indicate other major differences in these two horizons. It is also possible that the delta value was lower in the A_p horizon because this soil probably dries out to the wilting point only in the upper few inches of the profile. The delta values for the Tillamook, Winema, and Clatsop soils all fall within the range of 18.5 ± 2.0 me./100 g. The delta values for the Clatsop soil (19.5 and 20.5), a tideland soil containing minor amounts of soluble salts, are difficult to reconcile with current views of the conditions under which allophane develops. Aomine and Yoshinaga (3) comment on the "striking similarity of all clay fractions examined, regardless of depth in the profile and climatic conditions, indicated that volcanic ashes have produced allophane as a clay mineral in the well-drained state regardless of temperature, weathering time, vegetation, and ash origin". It would, then, appear that good drainage, to facilitate the removal from the profile of mono- and divalent metal cations, is a prerequisite to allophane formation. This is far from being the case for the Clatsop soil.

Presumably, then, the allophane in this soil was inherited rather than formed in place. There does not appear to be any information in the literature regarding the diagenesis of allophane when it is removed to a marine environment. The data at hand would indicate that it is rather stable in such an environment.

The free iron oxide removal method used in this study was somewhat more severe than that used by Aomine and Jackson (2) and could have had an adverse effect on the delta value. To evaluate this possibility, the A_p horizon of these five soils was taken through organic matter removal, iron oxide removal, boiling Na_2CO_3 dispersion, etc., using Jackson's (28, p. 57) iron removal method. Table 9 presents a comparison of the delta values obtained from the two sets of samples. It is immediately apparent that the difference in iron removal severity has a pronounced effect upon the delta value, although the effect is both positive and negative. For the Nehalem soil the more severe iron removal method gave a value lower by 12.8 me./100 g., whereas, with the Clatsop soil, it gave a value higher by 10.9 me./100 g. These data would indicate the delta value is highly dependent upon the severity of iron removal treatments. This might indicate that the allophane in these soils is admixed with varying quantities of iron oxides, as part of the allophane admixed with the iron oxides would be

Table 9. Effect of Severity of Free Iron Oxide Removal
On Cation Exchange Capacity Delta Values

Soil	Depth Inches	Iron Removal Method	Pretreatment		Delta Value	A-B
			Acidic	Basic		
Astoria	0-9	A ^{15/}	1.9	10.7	8.8	-3.2
		B ^{16/}	16.6	28.6	12.0	
Nehalem	0-9	A	40.3	60.7	20.5	-12.8
		B	53.7	87.0	33.3	
Tillamook	0-7	A	26.6	43.9	17.3	8.3
		B	42.2	51.2	9.0	
Winema	0-12	A	18.5	35.5	17.0	9.3
		B	26.8	34.5	7.7	
Clatsop	1-6	A	19.6	38.1	18.5	10.9
		B	26.9	34.5	7.6	

15/ Method used for preparation of samples for mineralogical analyses; 4 extractions using 9 g. of $\text{Na}_2\text{S}_2\text{O}_4$ per extraction for 5 g. soil samples.

16/ Method of M. L. Jackson (28, p. 63); two extractions using 1 g. of $\text{Na}_2\text{S}_2\text{O}_4$ per extraction for 5 g. samples.

of colloidal size. Thus, the more iron oxides removed, the more colloidal allophane that would be removed without being in true solution. It is also possible that part of the allophane is more soluble in some of the soils. Some indication of the latter possibility is found in the data of Chao (14) who found the quantity of aluminum removed by iron oxide removal treatments varied with the soil. His values, expressed as Al_2O_3 , were 2.2 and 1.7 percent for Astoria and Tillamook, respectively.

Sodium Hydroxide Solubility

The presence of amorphous material in these soils had been established by the determination of cation exchange delta values. Therefore, it was decided to seek further information relative to their abundance. The method of Hashimoto and Jackson (27) was chosen for this purpose.

This procedure involves the boiling of organic matter-free, iron oxide-free, and boiling- Na_2CO_3 dispersed samples with 0.5 N NaOH for 2.5 minutes followed by NaOH washes. The boiling NaOH extraction removes amorphous aluminum and silicon oxides, which would include allophane, silica relics, etc., as well as gibbsite. The authors found that the layer silicates did not release significant quantities of silica and aluminum under these conditions. The quantitative estimation of the amount of amorphous material

present would be complicated by the presence of gibbsite which would also be dissolved by the NaOH treatment.

Neither X-ray diffraction nor differential thermal analysis indicated the presence of gibbsite in any of the soil samples. It was, therefore, assumed to be either absent or present in such minor amounts that it could be ignored. It is felt that $\text{SiO}_2/\text{Al}_2\text{O}_3$ molecular ratios in the NaOH extract would give little or no useful information. Rather than $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of the NaOH extract, it was felt that the loss in weight of the samples would give the most useful information. This loss in weight was expressed as a percentage of the organic matter- and iron oxide-free sample weight.

Weight losses of some reference minerals are given in table 7. As a result of one NaOH extraction, the montmorillonite lost 7 percent of its weight, while the kaolinite and illite each lost 3 percent of their weight. From this data it is not possible to say whether the material dissolved is an amorphous aluminosilicate impurity or from the very small size fraction of the minerals, since the attack of the NaOH on the layer silicates would be a function of crystal size. A second NaOH extraction of the montmorillonite did not cause any additional weight loss. Hence, in the case of this particular mineral, the loss in weight must be due to an amorphous aluminosilicate contaminant.

The Japanese allophane lost 58 percent while the Hawaiian sample lost 70 percent (table 7). The high value for the Hilo sample is probably due to its gibbsite content since X-ray diffraction analyses of the Hilo silt gave very intense gibbsite reflections. Second extractions of the 2 reference samples of amorphous material indicated that the first extraction very nearly completed the removal of amorphous aluminosilicates.

Table 8 presents the weight losses of some profile samples. These weight losses range from 8 to 25 percent. The higher value for the Tillamook soil would represent one-fourth of the organic matter-free, iron oxide-free weight of the soil, which is certainly a very considerable portion not only of the inorganic portion but of the whole soil as well. There does not appear to be much by way of profile trends in these data, although the values for both the Astoria and Winema increase by 6 to 8 percent from the first to the second horizon. The weight losses of the two Tillamook samples were appreciably greater than those of the other samples, excepting the 8 to 12 inch depth of the Clatsop.

Differential Thermal Analysis

Both the delta value determinations and the solubility weight losses have indicated the presence of appreciable quantities of amorphous materials. The delta values had

indicated the presence of the Ando type of allophane. Differential thermal analyses offered the possibility of evaluating the presence of allophane A and B which has been reported in New Zealand soils (19).

To gain some familiarity with the equipment and also to evaluate its sensitivity, montmorillonite 11 (untreated, ground to 40 mesh) was run at various dilutions. Montmorillonite was used for this preliminary work since prior X-ray diffraction analyses had indicated it as the dominant mineral in these soils. The results indicated that the intensities of the low temperature endothermic peaks at 15, 30, 45, 75 and 100 percent montmorillonite dilutions were linear functions of the quantity of montmorillonite present. The peak temperature increased from 165 to 192°C. with increasing proportions of montmorillonite. It was observed that the low temperature endothermic reaction was much more intense with montmorillonite 24 than montmorillonite 11. It appeared that the 30 percent montmorillonite was the minimum that would still show the high temperature exothermic effects. It was then assumed that 45 or probably 60 percent would be the minimum amount of soil that could be used because of the dilution effect of the sands and silts present. The samples used were portions of samples pretreated for delta value determination.

Figures 7 and 8 show the differential thermograms that

were obtained. The Astoria 0 to 9, Clatsop 1 to 8, and Nehalem 0 to 9 inch depths were run with 55 percent of alundum diluent. The low temperature endothermic peaks were relatively small (5 to 9 percent of the chart width) and the 680°C. endothermic peak was very small (1 percent of the chart width). In spite of the very small size of the high temperature endothermic peak, it was rather well defined. The remaining samples were run with only 40 percent dilution, or conversely, 60 percent sample. With this decrease in alundum content, the samples sintered so badly that it was necessary to lift off the block, after removing the alundum from the reference thermocouple cavity, and crack the fused sample somewhat in the manner of cracking a nut. This, of course, had to be done with extreme care to avoid breaking the thermocouples. The base-line drift increased appreciably with the 40 percent alundum diluted samples as compared to the 55 percent dilutions. Because of the problem of sintering, it was not feasible to use a larger sample to alumina ratio. It may be noted in figures 7 and 8 that in most cases the base-line drift is upward, i.e., on the exothermic side of the starting point, but in some cases it is downward. It was observed that the downward drift of the base-line was always associated with the number 3 cavity. The exact reason for this situation was not clear.

The patterns all displayed low temperature endothermic

peaks indicative of expanding 2:1 type layer silicates and/or amorphous aluminosilicates. The shape of this peak in general is suggestive of those of montmorillonites (22) rather than amorphous materials (19, 6). However, there appeared to be some real differences between samples. In the case of the Astoria A_p horizon (figure 8), the high temperature shoulder of this peak returns part way to the base-line, then flattens out and only gradually approaches the base-line. The line does not level off at the base-line, but continues to rise, indicating that an exothermic reaction has taken place. This 300 to 335°C. exothermic peak is accentuated in the Tillamook A_p . It is also indicated in the Nehalem and Clatsop A_p horizons, the Nehalem 9 to 17 inch depth and the Astoria 9 to 23 inch depth. This exothermic reaction just after the low temperature endothermic peak is typical of allophane (19).

The question arises of whether the 300 to 335°C. exothermic reaction could also be due to organic materials not removed by the H_2O_2 treatments. Fieldes (19) reports that the H_2O_2 treated allophanic volcanic ash samples that he studied exhibited exothermic peaks due to organic matter in the 400 to 700°C. range. Considering that these samples were treated with 70 ml. of 30 percent H_2O_2 , it would not be expected that more than very minor amounts of organic matter would remain. On the basis of Fieldes' differential

Figure 7. Differential Thermograms of Montmorillonite and of Certain Nehalem and Clatsop Profile Samples

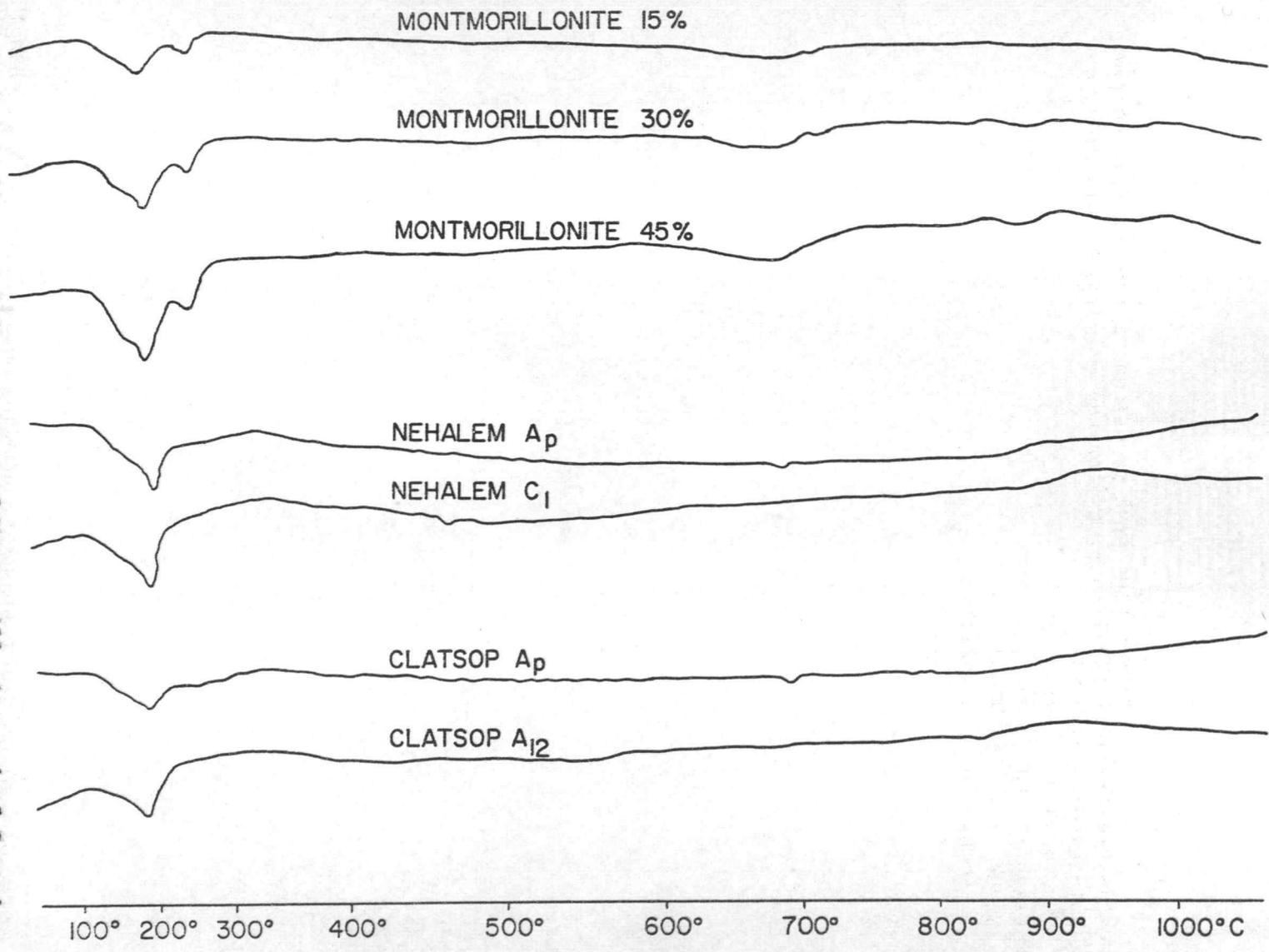
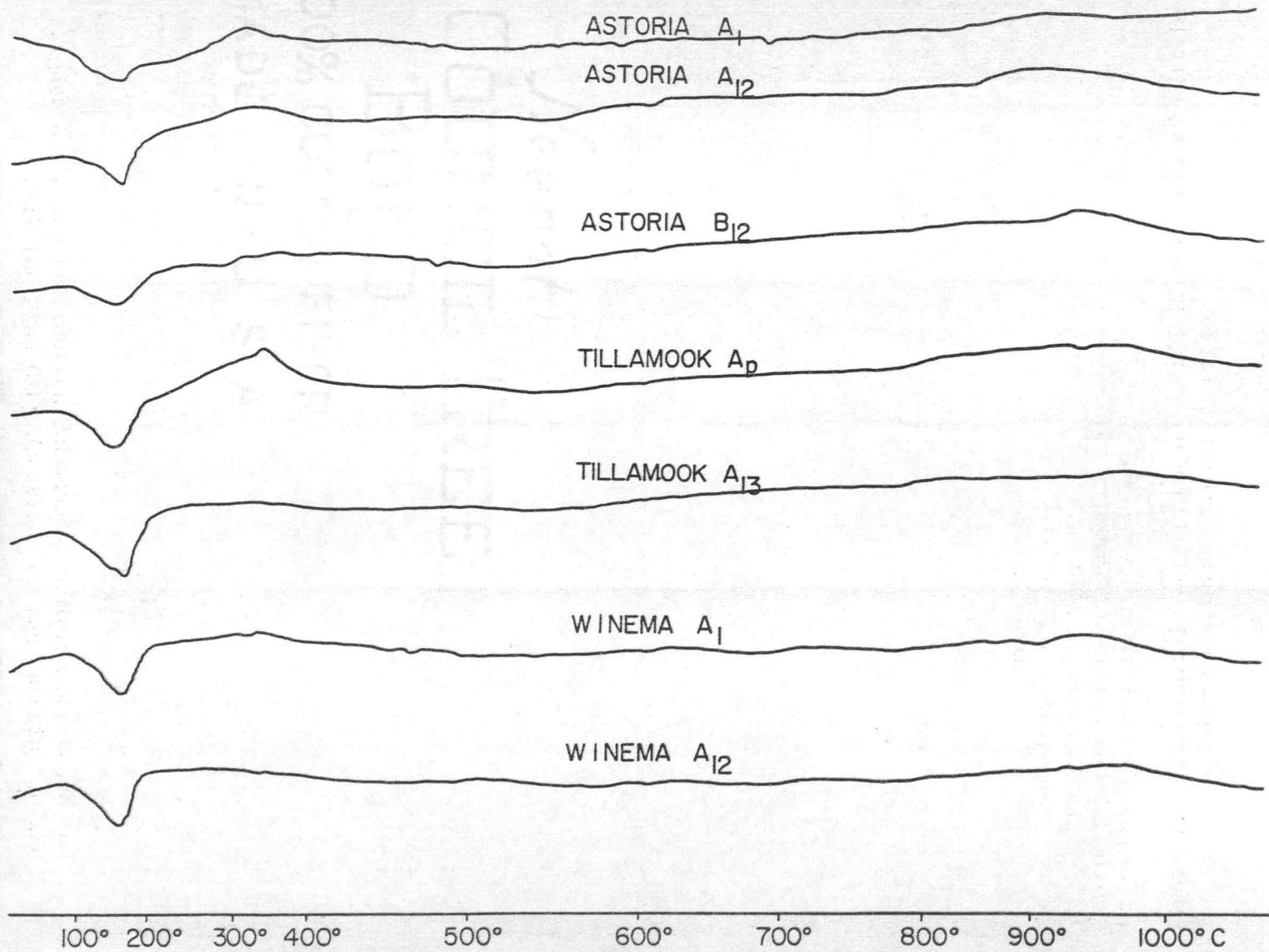


Figure 8. Differential Thermograms of Some Profile Samples From the Astoria, Tillamook, and Winema Soils



thermograms it appears that the 300 to 335°C. exothermic peak is probably due to amorphous materials rather than organic matter.



ADVANCE BOND

ARLINGTON, VIRGINIA

GENERAL DISCUSSION

MINERALOGICAL, CHEMICAL, AND FERTILITY RELATIONSHIPS

The Problem and Approach

A number of unexplained chemical properties and fertility responses have been noted in certain coastal soils. A detailed study of the clay mineralogy was undertaken to determine if a relationship could be established between the clay mineralogy of these soils and their chemical properties and fertility responses.

The results of the individual portions of the study have been discussed in the preceding sections. In the following sections, the results are summarized and discussed on the basis of the individual soil.

Astoria Soil

The Astoria soil has a fairly complex suite of layer silicates containing montmorillonite, chlorite, illite, kaolinite and possibly vermiculite. Information on the relative quantities of these minerals is limited to the results of X-ray diffraction of parallel-orientated specimens. Some inferences can be drawn from the intensities of the various peaks, but such things as the amount and type of interstratification, the complementary suite of minerals present, the amounts of amorphous inorganic materials,

degree of crystal perfection, etc. have a very profound affect on the resulting intensities. These factors should be kept in mind in considering the intensities of the peaks on X-ray diffraction patterns of parallel-oriented specimens. Roughly speaking, then, the intensities of the montmorillonite and chlorite (and vermiculite?) peaks are approximately equal. The montmorillonite and illite are interstratified to such an extent that nothing can be said about the amount of illite present. The amount of kaolinite is probably much less than the quantity of montmorillonite or chlorite present. No profile trends are apparent except the decrease in resolution of montmorillonite with depth in the fine clay fraction. This would indicate a corresponding increase of interstratification. Heat treatments indicated that there was a very considerable amount of a montmorillonite intergrade present as evidenced by a failure of the montmorillonite to collapse to 10 \AA upon heating to 300°C . In the case of the amorphous aluminosilicates, there are distinct profile differences (table 8). The delta values show a sharp increase from the A_{12} (9 to 23 inch) to the B_{11} (33 to 43 inch) horizon while the solubility weight losses (table 8) indicate an increase in the amorphous aluminosilicates between B_{11} (23 to 33 inch) and the B_{12} (33 to 43 inch) horizon. Delta values of the A_{1p} were evaluated after iron oxide treatments of differing severity. It was

found that this delta value was decreased by the more severe technique. This might indicate that the allophane of this soil is more soluble than some of the other soils.

Differential thermal analyses (figures 7 and 8) gave some indication of the presence of amorphous materials in the A_p (0 to 9 inch) and the A_{12} (9 to 23 inch) horizons but not in the B_{12} (33 to 43 inch). The instrument was not sufficiently sensitive to determine whether this amorphous material would be the equivalent to allophane A or allophane B described in New Zealand (19).

The presence of appreciable quantities of amorphous aluminosilicates in this soil has been established. It is, therefore, appropriate to consider what relation it has to the chemical properties of this soil. The low pH of 4.7 found for the A_p is comparable to the value of 4.5 given by Kanno (32) for volcanic ash soils. A low pH is thought to be a prerequisite for, or coincident with, the accumulation of appreciable quantities of allophane. The base saturations are certainly comparable with those of the Japanese Ando soils (32). The low pH is presumably a result of intensive leaching, which is the condition under which allophane forms in Japanese volcanic ash soils. In view of the simultaneous occurrence of amorphous materials and montmorillonite in this soil, some recent conclusions of Grim (24) are of interest. He observed the alteration products of

Tertiary to Recent volcanic ash in Japan. He found that some of the volcanic materials have very low contents of MgO (less than 0.5%) and these are the ones that alter to kaolinite, halloysite, and allophane. With substantially higher contents of MgO, montmorillonite is the alteration product.

The exchange capacity of this soil is in the lower end of the range of cation exchange capacities normally found for allophanic soils (32, 49, 2). However, higher values have been found for other locations of this soil series (appendix I).

The curve showing the calcium release versus calcium saturation of the Hilo subsoil does not appear very similar to the release curves of the soils (figure 2). This is probably because the exchange complex of the Hilo sample is completely dominated by amorphous material, whereas, in the soils the amorphous material does not completely dominate the exchange complex. The high concentration of calcium in equilibrated extracts of the Hilo indicates that amorphous material is the explanation of the high availability of calcium in the Astoria and Tillamook soil at such a low base saturation.

The potassium response on this soil was very marked. This was due in part to the high potassium demands of legumes, as 5 harvests were taken per year, although to a much

greater extent it represents the low potassium supplying power of the soil. In a recent study of various methods of estimating potassium availability, Gardner (20) found, that of the coastal and Willamette Valley soils used in his study, the Astoria soil had the lowest level of exchangeable potassium as well as the lowest rate of release of slowly available potassium. This would be related to the scarcity of potassium bearing minerals. However, both illite and feldspars were identified in this soil.

If there were appreciable amorphous materials in this soil, it might be expected that there would be a high rate of phosphorus fixation. If such a situation existed, one would have expected a yield response to phosphorus fertilization. However, essentially no yield response occurred as a result of phosphorus applications. The reason for this situation is not entirely clear. The chemical reactivity of the amorphous material in this soil would appear to be low as evidenced by the low delta values. Fieldes (19) has concluded from studies of allophane in volcanic ash soils that where clay is formed by weathering of ash in the presence of colloidal humic material, an appreciable amount of alumina may be bound in a stable organic complex limiting the possibility of coprecipitation of alumina and silica. This does not mean that the formation of allophane is restricted; on the contrary, the aluminum-organic matter

relationship reduces the loss of aluminum by leaching. The silica remains as the discrete hydrous oxide. The combination of coprecipitated aluminum and silicon plus discrete silicon oxides is described by Fieldes (19) as allophane B. The combination of organic matter with aluminum would reduce the precipitation of aluminum phosphates.

The high molybdenum availability observed on this soil apparently results from the combination of liming an acid, high organic matter soil. This has been observed by Herbert Howell (personal communication) in studies of minor element balance in animal nutrition at the John Jacob Astor Experiment Station.

Nehalem Soil

In this soil the mineralogy of the clay fraction appears to be very simple as only montmorillonite was identified (figure 4). This was unexpected since Gardner (20) had shown that this soil not only had a high level of exchangeable potassium as is shown in table 3, but had a very high rate of release of slowly available potassium. In the other soils which he studied, a high release rate for slowly available potassium was associated with the presence of a mineral giving a 10 Å X-ray diffraction line. An additional indication of the high potassium status of this soil is that no response to potassium has yet been observed in the field

experiment.

Feldspars were identified in both the sand and silt fractions. The feldspar reflection in this soil was a single peak rather than a doublet as was the case with the Astoria soil. However, the results of the X-ray diffraction analyses did not provide information as to the specific feldspar minerals present. Although, in view of the low release rate for slowly available potassium that Gardner found for silt size potassic feldspars, it seems unlikely that they are the major source of the high release of slowly available potassium in this soil.

On the basis of the potassium contents of montmorillonites (23, p. 371) and the negligible potassium release from reference montmorillonites (20), it seemed unreasonable that this potassium was coming from the montmorillonite, which is the only mineral identified in the clay fraction. An organic matter-free, iron oxide-free silt fraction of the A_p horizon was subjected to the HCl leaching method of Gardner (20). This resulted in a considerable amount of potassium released which pointed to the silt fraction as the possible source of the potassium in this soil. It is apparent that there must be a potassium bearing mineral present in this soil which is releasing potassium at a fairly high rate. However, its nature was not discovered.

The amount of amorphous aluminosilicate removed from

this soil by the boiling NaOH treatment was appreciable (table 7). Twelve percent of the organic matter-free, iron oxide-free weight of the samples was removed by the treatment. While there is no reason to suspect a relationship between the amorphous aluminosilicate and the high potassium release, it is something which should be evaluated in the future.

The high delta values (table 8) indicated that the amorphous material in this soil is very reactive. In spite of this, however, no phosphorus response was found in the field experiments.

The lack of a lime response in this soil is due to the relatively high level of exchangeable calcium present in the soil. It was somewhat surprising to find a pH of 5.2 with a calcium saturation of 50 percent.

Tillamook Soil

Montmorillonite was the dominant layer silicate identified in this soil. Lesser quantities of kaolinite occurred in the coarse clay fraction. Traces of illite were found in some horizons. Feldspars were also present although possibly in slightly smaller amounts than in the Nehalem.

Contrary to the situation with the other 2 field experiments, forage on the Tillamook site showed very poor seedling vigor. The second harvest was taken from the

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Nehalem soil at the time of the first harvest on the Tillamook soil. The first year's yield data (presented in appendix IX) shows a significant response to lime, but not to phosphorous or potassium. This appeared to be largely a result of the very large amount of organic matter present (20 percent). This was indicated by the series of nitrogen rate plots adjoining the main experiment. The plots receiving nitrogen, irrespective of other fertilization, grew vigorously and were ready to harvest at the time of the first cutting of the Nehalem plots. In retrospect, it now appears that a blanket application of nitrogen should have been applied to the experiment at the time of establishment and possibly again the following spring. While it is unusual to apply nitrogen fertilizer to a legume-grass mixture, it is also unusual to have a mineral soil with 20 percent organic matter. The carbon:nitrogen ratio of this soil is about 15. Microbiological activity usually shows a considerable increase as a result of the pulverization and mixing that occurs in seedbed preparation. This increased microbiological activity results in competition with the forage for available nutrients. This operates to the detriment of the establishment of a new seeding.

By the second year after establishment, the stimulated microbiological activity has probably subsided and in addition the nitrogen fixation by clover root nodules has

apparently increased to the extent that the forage production was being limited by other nutrients. The first 1960 harvest indicated a significant response to potassium and phosphorous as well as to lime, which was a marked difference from the previous year. The effect of the fertilizer treatments on botanical composition was very apparent.

The delta values for this soil are slightly below those for the Nehalem (table 8) but the NaOH weight losses are twice as high. About one-fifth of the organic matter-free, iron oxide-free weight of this soil was shown to consist of amorphous materials. The high content of amorphous material is probably a very important factor in causing the high organic matter accumulation (19, 32).

The differential thermograms indicated more amorphous material in the A_{1p} of the Tillamook than in any other sample.

The Tillamook released slightly less Ca+Mg to equilibrium solutions than did the Astoria soil. It is possible that it reflects amorphous materials of a different nature.

It then appears that the large organic matter content of this soil has immobilized the plant nutrients added and was, thus, responsible for the initial lack of fertilizer responses. This effect is due both to chemical reactions and increased microbiological activity.

Summary

The high concentration of calcium in equilibrated extracts in the case of the Astoria and Tillamook appears to be largely due to the amorphous inorganic materials present. Thus, in spite of the very low base saturation and pH values of these two soils, the yield responses to lime applications were not marked. Furthermore, the responses that have occurred have been at low rates of applied lime. The yield increases occasioned by the lime treatments were due in part to increased microbial production of nitrate.

The general lack of a phosphorus response was not anticipated on the basis of the bicarbonate extractable phosphorus, since in the absence of experimental data for these soils it was necessary to use information on yield data obtained on Willamette Valley alluvial soils.

The marked response of the Astoria soil to potassium was associated both with a high forage yield and with a low release of slowly available potassium. The high rate of release of slowly available potassium in the case of the Nehalem soil is due to the presence of one or more of a potassium bearing mineral, the identity of which was not discovered.

It is apparent that a definite and definable relationship exists between soil mineralogy, soil chemical properties, and fertility responses. This relationship is

confounded in the presence of very high organic matter contents and may not be readily apparent. It is also evident that the understanding of this relationship requires a very detailed knowledge of the mineralogy of the soils involved.

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Chas. L. BROWN Paper

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ADVANCE BOND



APPENDIXES

APPENDIX I

Soil Test Information From Survey Samples of the Ap Horizon of Nine Coastal Soil Series

Lab. No.	County	pH	Lime Requirement	P	Exchangeable Cations				C.E.C.	Base Sat.
		H ₂ O	Tons/Acre	PPM	Na	K	Mg	Ca	me./100 g.	Percent
		1:1								
Astoria Soil										
R8160	Clatsop	5.1	7.0	3.4	-	0.9	2.8	4.0	45.5	16.9
R8163	Clatsop	5.0	7.5	2.5	-	1.0	1.9	1.6	47.7	9.4
R8167	Clatsop	4.8	6.0	10.8	-	0.4	2.7	1.9	-	-
R8171	Clatsop	5.0	5.5	-	Tr	0.4	1.1	1.5	42.5	7.1
Nehalem Soil										
R8162	Tillamook	5.3	4.0	3.8	-	0.2	6.9	17.8	40.5	61.7
R8159	Clatsop	5.4	5.5	9.0	-	0.5	1.1	3.7	33.9	15.6
R8151	Tillamook	5.6	4.0	4.2	-	0.6	7.4	20.4	55.2	51.4
R8150	Tillamook	5.9	4.0	2.7	-	0.2	7.6	18.5	50.1	52.5
R8141	Lincoln	5.6	4.0	3.0	-	0.7	7.0	12.5	35.5	56.9
R8140	Lincoln	5.5	5.0	5.5	-	1.4	9.7	14.6	43.8	58.7
R8139	Lincoln	5.5	5.0	5.0	-	1.3	9.9	13.8	49.8	50.2
R7376	Clatsop	6.0	1.5	6.0	0.6	0.4	7.6	14.4	22.4	89.3
R7371	Clatsop	5.8	2.0	8.6	0.3	0.7	8.8	8.5	19.0	91.3
R8445	Tillamook	5.8	3.5	9.5	-	0.7	8.5	22.2	48.0	65.1

ADVANCE BOOK

APPENDIX I (Continued)

Lab. No.	County	pH H ₂ O :1:1	Lime Re- quirement :Tons/Acre:	P PPM	Exchangeable Cations: Na K Mg Ca	C.E.C.	Base Sat. Percent			
					me./100 g.					
Tillamook Soil										
R8135	Lincoln	4.8	6.5	14.2	-	2.2	4.8	7.6	49.8	29.3
R8136	Lincoln	5.4	6.0	32.7	-	0.7	3.0	8.3	49.1	24.4
R8137	Lincoln	5.6	7.0	6.5	-	0.9	1.5	3.6	44.4	13.5
R8146	Tillamook	5.3	6.5	1.5	-	0.3	0.5	1.3	50.8	4.1
R8148	Tillamook	5.5	6.0	1.7	-	0.2	0.9	2.7	57.2	6.6
R8149	Tillamook	5.6	6.0	2.0	-	0.3	1.3	3.5	56.7	9.0
Winema Soil										
R8144	Tillamook	5.2	6.0	3.4	-	1.4	4.3	4.1	40.7	24.1
R8143	Tillamook	5.3	6.0	2.5	-	0.6	3.0	3.7	45.7	16.0
R8446	Tillamook	5.2	6.0	7.0	-	1.6	3.0	5.5	38.5	26.2
Clatsop Soil										
R8161	Clatsop	5.1	6.0	2.0	-	0.6	10.3	4.4	42.5	36.0
R8164	Clatsop	4.8	7.0	3.2	-	0.2	3.8	3.9	35.9	22.0
R8165	Clatsop	5.0	6.0	4.5	-	0.2	3.2	6.4	39.5	24.8
R8168	Clatsop	5.0	6.5	4.5	-	0.6	10.5	2.6	47.0	27.0

APPENDIX II

Profile Descriptions

Astoria Soil (Brown Latosol)

Location: Clatsop County, Oregon. John Jacob Astor Branch Experiment Station. About 4 miles southeast of Astoria. Near the midpoint of the line between sections 22 and 27, T 8 N, R 9 W.

<u>Horizon</u>	<u>Depth (inches)</u>	<u>Description</u>
A11	0-9	Very dark brown (10YR 2/3) silt loam, brown (10YR 4/3 dry); strong, very fine, granular structure; friable, plastic, sticky; many roots; many very fine pores; few, very fine concretions; pH 4.8; lower boundary gradual and smooth.
A12	9-23	Very dark brown (10YR 2/3 moist) silty clay loam; strong, very fine, subangular blocky structure; friable, plastic, sticky; many roots; many very fine pores; few, very fine concretions; pH 5.0; lower boundary gradual and wavy.
B11	23-33	Dark yellowish brown (10YR 3/4 moist) silty clay loam; moderate, fine and very fine, subangular blocky breaking to strong, very fine, granular structure; friable, plastic, sticky, many roots; common, very fine, tubular pores; few very fine concretions; common very thin clay skins; pH 5.2; lower boundary gradual and wavy.
B12	33-43	Dark yellowish brown (10YR 3/4 moist) silty clay; moderate, very fine, subangular blocky structure; friable, plastic, sticky; common roots; common, very fine, tubular pores; many very thin clay skins; pH 5.2; lower boundary clear and irregular.

<u>Horizon</u>	<u>Depth (inches)</u>	<u>Description</u>
B2	43-60	Dark yellowish brown (10YR 4/4 moist) clay; moderate, coarse breaking to moderate, fine, subangular blocky structure; firm, plastic, sticky; common roots; few, very fine, tubular pores; many thin clay skins; pH 4.6.

Nehalem Soil

Location: Southwest corner of the Nehalem soil fertility plots on the Tillamook Naval Air Force Base.

<u>Horizon</u>	<u>Depth (inches)</u>	<u>Description</u>
Ap	0-9	Dark yellowish brown (10YR 3/4) moist, brown (10YR 5/3) dry, silt loam (but almost silty clay loam), strong fine and very fine subangular blocky structure, friable, slightly sticky, slightly plastic, abundant roots, abundant fine and very fine interstitial pores, pH 5.2 (chlorphenol red), lower boundary clear and smooth.
C1	9-17	Dark yellowish brown (10YR 3.5/4) moist, silt loam (but almost silty clay loam), moderate medium prismatic breaking to strong fine subangular blocky structure, friable, slightly sticky, slightly plastic, abundant roots, abundant fine tubular pores, few medium and coarse tubular pores, coatings on peds and pores are 10YR 3/4, pH 5.4 (chlorphenol red), lower boundary, gradual and smooth.
C2	17-37	Dark yellowish brown (10YR 3.5/4) moist, silty clay loam, moderate coarse prismatic breaking to strong medium subangular blocky structure, friable, plastic sticky, common roots, abundant fine tubular pores, pH 5.6 (chlorphenol red), few medium and coarse tubular pores, lower boundary gradual and smooth.

<u>Horizon</u>	<u>Depth (inches)</u>	<u>Description</u>
C3	37-54	Dark yellowish brown (10YR 3.5/4) moist, silty clay loam, weak coarse prismatic breaking to moderate fine and medium subangular blocky structure, friable, plastic, sticky, few roots, abundant fine and very fine tubular pores, few medium and coarse tubular pores, few, faint fine mottles, pH 5.6 (chlorphenol red).

Tillamook Soil

Location: Field Experimental Site on the Tillamook Naval Air Force Base.

<u>Horizon</u>	<u>Depth (inches)</u>	<u>Description</u>
Al _p	0-7	Black (10YR 1.2) moist, silt loam, moderate fine and very fine subangular blocky structure, friable, slightly sticky, slightly plastic, abundant roots, abundant fine and very fine interstitial pores, lower boundary abrupt and smooth.
Al ₂	7-16	Black (10YR 1/2) moist, silt loam, strong medium and fine subangular blocky structure, friable, slightly plastic, slightly sticky, abundant roots, abundant fine and very fine interstitial pores, lower boundary clear and wavy.
Al ₃	16-39	Black (10YR 1/2) moist, silt loam, weak coarse prismatic breaking to weak medium and fine subangular blocky breaking to moderate very fine granular structure, friable, slightly plastic, slightly sticky, common roots, abundant fine and very fine tubular and interstitial pores, lower boundary clear and irregular.

<u>Horizon</u>	<u>Depth (inches)</u>	<u>Description</u>
B1	39-50	Very dark brown (10YR 2.5/3) moist, silty clay loam, moderate fine and very fine granular structure, friable, plastic, sticky, few roots, abundant fine and very fine tubular pores, few medium and coarse tubular pores, lower boundary clear and irregular.
B2	50-60	Dark yellowish brown (10YR 3/4) moist, silty clay loam, moderate medium to very fine subangular blocky structure, friable, plastic, sticky, few roots, abundant fine and very fine tubular pores, few medium and coarse tubular pores, few rounded pebbles.

APPENDIX III. Hilo Soil

Classification: Hydrol Humic Latosal - class 9.51 of the 6th approximation.

Parent Material: Volcanic ash.

Climate: 175-200 inches of rain.

Vegetation: Cleared from Ohio tree fern vegetation, now in sugar cane.

Physiography: Low undulating to rolling windward slopes of Mauna Kea. Slope 5% convex to East.

Elevation: 300 feet.

Drainage: Well drained but soils never dry out because it rains almost every day. Soil appears well aerated.

APPENDIX IV

Potassium Concentration in Equilibrium Extracts

From Three Field Experiments

Pounds K ₂ O per Acre	K Conc. Equil. Soln. moles x 10 ⁷ /l.	Exch. K me./100 g.	K Saturation Percent
Astoria ^{17/}			
0	2.6	0.16	0.42
100	3.0	0.17	0.46
200	4.2	0.23	0.60
Nehalem ^{18/}			
0	3.0	0.44	0.76
50	3.7	0.49	0.84
100	4.9	0.63	1.09
200	5.5	0.63	1.09
Tillamook ^{19/}			
0	3.3	0.47	1.02
60	3.3	0.49	1.06
120	3.2	0.59	1.28
240	3.8	0.63	1.37

17/ Cation Exchange Capacity = 38.1 me./100 g.

18/ Cation Exchange Capacity = 58.1 me./100 g.

19/ Cation Exchange Capacity = 45.9 me./100 g.

APPENDIX V

Effect of Lime, Phosphorus, and Potassium
on the Forage Yield of the Astoria Soil
(Total of Five Cuttings, Pounds Dry Weight
Per Acre)

		<u>1957</u>			<u>1958</u>		
		1) Lime by Phosphorus Factorial (K_2)					
		P H O S P H O R U S					
		0	1	2	0	1	2
	0			9110	0		7830
	1	9440	10580	9600	1	8280	9220
LIME	2	9710	10960	10800	2	9290	9520
	3	9790	11010	11100	3	9060	9230
	4			11720	4		9490

		2) Lime by Potassium Factorial (P_2)		
		P O T A S S I U M		
		0	1	2
	0			9110
	1	8650	9980	9600
LIME	2	9330	10100	10780
	3	9610	10760	11100
	4			11720

3) Fertilizer Treatments

<u>Lime T/A</u>	<u>P_2O_5 lbs/A</u>	<u>K_2O lbs/A</u>
$L_0 = 0$	$P_0 = 0$	$K_0 = 0$
$L_1 = 3$	$P_1 = 100$	$K_1 = 100$
$L_2 = 6$	$P_2 = 200$	$K_2 = 200$
$L_3 = 12$		
$L_4 = 24$		

APPENDIX VI

Analysis of Variance for 1958 Yield Data
From the Astoria Soil

1) Analysis of Variance

Source of Variation	D. F.	Mean Square	F
Total	53	-	-
Lime	2	219442	0.47
P	2	302690	0.65
LxP	4	469111	1.00
K	1	78476844	167.98**
LxK	2	1123506	2.40
PxK	2	528353	1.13
LxPxK	4	1989248	4.26**
Error	50	467174	-

2) Coefficient of Variation = 8.5 percent

APPENDIX VII

Effect of Lime, Phosphorus, and Potassium
on the Forage Yield of the Nehalem Soil ^{20/}
(Total of Three Cuttings, Pounds Dry Weight Per Acre)

1) Lime by Phosphorus Factorial (K_2N_0)

		P H O S P H O R U S				
		0	1	2	3	4
LIME	0	7,560	7,090	6,720	6,460	6,300
	1	7,880	7,670	7,560	7,560	7,330
	2	7,910	7,950	8,110	8,360	8,720
	4	7,050	7,620	8,280	9,050	9,930

2) Lime by Potassium Factorial (P_2N_0)

		P O T A S S I U M				
		0	1	2	3	4
LIME	0	7,830	7,720	7,560	7,360	7,110
	1	7,760	7,920	8,040	8,110	8,130
	2	7,410	7,850	8,240	8,580	8,850
	4	5,910	6,890	7,830	8,720	9,560

3) Fertilizer Coding

Lime T/A	P_2O_5 lb/A	K_2O lb/A	NH_4NO_3 lb/A
$L_0 = 0$	$P_0 = 0$	$K_0 = 0$	$N_0 = 0$
$L_1 = 2$	$P_1 = 60$	$K_1 = 50$	$N_1 = 30$
$L_2 = 4$	$P_2 = 120$	$K_2 = 100$	$N_2 = 60$
$L_4 = 8$	$P_4 = 240$	$K_4 = 200$	$N_4 = 120$

^{20/} The yield data presented is that calculated from the regression equation.

APPENDIX VIII

Analysis of Variance For 1959 Yield Data
From the Nehalem Soil

1) Regression Coefficients

(1)(2)	b_0	b_1	b_2	b_{12}	b_{11}	b_{22}
LxP	17.26	0.83	0.43	0.55	-0.32	0.11
LxK	17.55	0.14	0.78	-0.58	-0.29	-0.05
PxK	17.10	0.65	1.04	4.33	0.15	-0.15

2) Analysis of Variance

Coe- ff.	D.F.	LxP		LxK		PxK	
		M S	F	M S	F	M S	F
b_1	1	44.9972	6.93*	0.7674	0.12	11.0153	1.70
b_2	1	11.8778	1.83	22.9130	3.53	28.0215	4.31*
b_{12}	1	21.2015	3.26	8.7986	1.36	45.1016	6.95*
b_{11}	1	9.8389	1.52	6.6564	1.02	1.0225	0.16
b_{22}	1	1.1809	0.18	0.2226	-	0.9798	0.15
Error	54	6.4943	-	6.4934	-	6.4934	-

3) Coefficient of Variation = 14.9 percent

4) Treatment Levels

Coded Level	L	Uncoded Level			
		0	1	2	3
L	L	-2	-1	0	2
P	P	-2	-1	0	2
K	K	-2	-1	0	2

APPENDIX IX

Effect of Lime, Phosphorus, and Potassium on Forage
Yield of Tillamook Soil (Total of Two
Cuttings in 1959, One Cutting in
1960; Pounds Dry Weight Per Acre)

195919601) Lime by Phosphorus Factorial (K_2N_0)

P H O S P H O R U S

	0	1	2	3	4	0	1	2	4
LIME 0	6170	6350	6350	6190	5860	2270	3030	4430	--
LIME 1	6950	7160	7200	7080	6760	2760	4810	4330	5410
LIME 2	7390	7640	7720	7630	7370	2920	4430	4700	5140
LIME 4	7250	6570	7720	7710	7530	--	4542	4810	4760

2) Lime by Potassium Factorial (P_2N_0)

P O T A S S I U M

	0	1	2	3	4	0	1	2	4
LIME 0	6620	6450	6600	7090	7900	--	3350	4430	--
LIME 1	7130	6850	6890	7270	7970	3990	4380	4430	5190
LIME 2	7600	7210	7150	7420	8010	4810	5520	4700	6000
LIME 4	8430	7820	7540	7590	7970	--	4700	4810	--

3) Fertilizer Levels

Lime	T/A	P_2O_5	lb/A	K_2O	lb/A	NH_4NO_3	lb/A
L_0	= 0	P_0	= 0	K_0	= 0	N_0	= 0
L_1	= 3	P_1	= 60	K_1	= 60	N_1	= 30
L_2	= 6	P_2	= 120	K_2	= 120	N_2	= 60
L_4	= 12	P_4	= 240	K_4	= 240	N_4	= 120

APPENDIX X

Analysis of Variance For Yield Data

From the Tillamook Soil

1959

(1)(2)	1) Regression Coefficients					
	b_0	b_1	b_2	b_{12}	b_{11}	b_{22}
LxP	16.43	0.73	-0.01	0.08	-0.36	-0.18
LxK	15.22	0.50	0.22	-0.23	-0.04	0.35
PxK	15.54	0.42	0.25	0.50	0.35	0.18

Source	D. F.	2) Analysis of Variance					
		LxP		LxK		PxK	
		MS	F	MS	F	MS	F
b_0	1	34.5477	9.14**	9.5588	2.53	4.6706	1.24
b_1	1	0.0099	-	1.7363	0.46	1.6553	0.44
b_{12}	1	0.4440	-	1.3690	0.36	0.5753	-
b_{11}	1	12.1973	3.23	0.1468	-	5.5598	1.47
b_{22}	1	3.8935	1.03	9.7221	2.57	1.4965	0.40
Error	54	3.7807	-	3.7807	-	3.7807	-

3) Coefficient of Variation = 12.5 percent

4) Treatment Levels

Coded Level		Uncoded Level			
		0	1	2	3
L	-2	-1	0	2	
P	-2	-1	0	2	
K	-2	-1	0	2	

APPENDIX X Continued

1) Analysis of Variance

Source of Variation	D. F.	Mean Square	F
Total	83	-	-
Replications	2	52.82	2.11
Treatments	27	145.05	5.79**
L	2	216.68	8.65**
P	2	476.02	19.01**
K	3	113.46	4.53**
LxP	4	39.26	1.57
LxK	3	9.30	0.37
PxK	1	38.17	1.52
Error	54	25.04	-

2) Coefficient of Variation = 15.6 percent

APPENDIX XI

Available Nitrate and Nitriafiable Nitrogen Expressed as
Parts Per Million of Dry Soil^{21/}

Lime Rate	L ₀ (0 ton)		L ₂ (6 ton)		L ₄ (24 ton)	
Replication:	NO ₃ -N	Nit.-N	NO ₃ -N	Nit.-N	NO ₃ -N	Nit.-N
I	5.0	6.2	3.7	6.0	1.0	19.2
II	1.5	5.4	1.7	12.1	1.4	28.2
III	3.1	4.5	1.7	7.5	2.1	10.5
Average	2.6	4.8	2.2	7.7	1.4	17.4
Difference of NO ₃ -N & Nit.-N	2.2		5.7		16.0	

^{21/} Samples were taken subsequent to the third harvest (1958) from plots receiving phosphorus and potassium rates of 200 pounds of P₂O₅/acre and 200 pounds of K₂O/acre, respectively.