# EVALUATION OF SPODIC HORIZON CRITERIA, AND CLASSIFICATION OF SOME MICHIGAN SOILS

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#### ABSTRACT

# EVALUATION OF SPODIC HORIZON CRITERIA, AND CLASSIFICATION OF SOME MICHIGAN SOILS

### by David A. Lietzke

Twenty Michigan soils representing 12 series were used to test three extraction procedures in order to evaluate the spodic horizon criteria and the Spodosol classification.

The extraction procedures used were: the citrate-dithionite procedure of Jackson and Mehra, the acid ammonium oxalate procedure of McKeague and Day, and the pyrophosphate-dithionite procedure of Franzmeier et. al.

Iron and aluminum were determined in the soils by these extraction procedures. Extractable carbon was also determined on the pyrophosphate-dithionite extracts. The oxalate procedure, which differentiates between amorphous and crystalline forms of iron in spodic horizons, extracted less iron than the other two procedures. The oxalate extraction procedure was the easiest of the three to use.

The citrate-dithionite and pyrophosphate-dithionite procedures extracted comparable amounts of iron from spodic horizons. Both of these procedures fail to differentiate between amorphous and crystalline forms of

iron. This fact is readily evident when the extractable iron contents increase along with increasing clay content. In contrast, the oxalate extractable iron values increase only slightly with increasing clay contents. The oxalate procedure generally extracted the largest quantity of aluminum from spodic and ortstein horizons; the citrate-dithionite procedure extracted the least, and the pyrophosphate-dithionite extractable values generally fell in between. However, some pyrophosphate-dithionite extractable aluminum values equaled or exceeded the oxalate values for a particular horizon.

The current usage of pyrophosphate-dithionite extractable carbon in the spodic horizon criteria does not give a major advantage over using total carbon values in the soils studied. Proposed changes in spodic horizon criteria are suggested which utilize total carbon along with either citrate-dithionite or pyrophosphate-dithionite iron and aluminum values. Criteria are also proposed using total carbon plus oxalate extractable iron and aluminum.

All three procedures, although resulting in different amounts of extractable iron and aluminum, result with the

proposed criteria in the same placement of the soils as spodosols or other soils in this study in nearly all cases. (Oakville exceeds the minimum amount of Fe+Al+C by all but the current classification criterion. Oxalate extraction qualified the 52 Omega profile but not the other criteria.)

New analysis procedures using atomic absorption spectroscopy for iron and aluminum determinations and an induction furnace carbon analyzer greatly speeded up the determinations of these elements, and produced more reproducible results.

A Quick Test was devised and tested in both the laboratory and in the field. The test utilizes the formation of a colored solution when a spodic horizon sample is treated with a saturated pyrophosphate solution. Experience to date with this test enables a more positive identification of spodic horizons in the field without the necessity of using cumbersome laboratory procedures. The Quick Test, with other field criteria of the spodic horizon, sorted out the Haplohumods and Haplorthods from other soils.

# EVALUATION OF SPODIC HORIZON CRITERIA, AND CLASSIFICATION OF SOME MICHIGAN SOILS

Ву

David A. Lietzke

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#### I. INTRODUCTION

The Comprehensive Soil Classification System relies heavily on chemical data for the separation of Spodosols into Great Groups and Subgroups. This study was undertaken to test the spodic horizon criteria and the Spodosol classification system on Michigan soils. Different extraction procedures were also to be evaluated in order to determine the advantages and disadvantages of each, and to determine if an easier and simpler procedure would accomplish the same end result as the present somewhat cumbersome pyrophosphate-dithionite extraction procedure.

The soils in this study run the gamut from showing some evidence of podzolization to the strongest development, providing a thorough test of the spodic horizon criteria and classification.

The other objective of this study was to develop a rapid procedure whereby a spodic horizon could be more positively identified in the field using criteria other than the soil color.

Still another objective, was to classify the Michigan soils in this study in the Canadian soil classification system, as a means of comparing the two classification schemes.

#### II. LITERATURE REVIEW AND METHODS USED

# A. Amorphous Materials in Soils - Their Composition and Methods of Removal

Amorphous substances have received researchers' attention in recent years after X-ray analysis of some clays produced fuzzy unclear diffraction patterns. DTA analyses indicated the presence of hydrous oxides (49). The removal of these substances resulted in much sharper X-ray patterns. Many methods (2, 21, 37, 47, 73) were proposed to remove this amorphous material before any mineralogical investigations. However, studies revealed in most cases, that once the amorphous materials were removed from the clay, the CEC (cation exchange capacity) decreased (21). Research on the composition of the amorphous materials has been reviewed by Mitchell et al (49) along with their own laboratory results in a broad study of amorphous inorganic materials in soils.

White (79) defined allophane as "...any amorphous substance which may be present in clay minerals". Most mineralogists restrict the definition of allophane to combinations of amorphous alumina and silica (58).

Apparently (58) gibbsite is the only important hydrated

aluminum oxide that occurs in soils, as either amorphous material or as very fine crystals. Amorphous aluminum oxide or hydroxide does not form discrete particles, but silica stabilizes this amorphous aluminum oxide or hydroxides as allophane which coats soil particles.

DeMumbrum et al (22) isolated and characterized some soil allophanes from a wide range of Wisconsin soils. They treated the soils to destroy the organic matter and then extracted to remove the amorphous materials including allophane. They found the inorganic allophanes to be mostly hydrous aluminum silicates, which are probably the result of weathering processes. The presence of Al(OH)3 in amorphous form was also suggested.

Much of the amorphous silica in soils is a direct influence of the parent material, especially in soils of volcanic origin. Some amorphous silica is also the result of plant and insect activities, for example, silica also occurs (49) as opal phytoliths in the amorphous fraction.

Amorphous aluminous materials occur in most soils in amounts varying from traces to large quantities. It occurs as oxides or hydrous oxides, organic-aluminum complexes, and as allophane when associated with amorphous silica (49).

Iron oxides and hydroxides are among the most common and abundant of the non-crystalline clay components.

Iron oxides can occur as discrete larger particles and coatings in the soil, and are readily observed with a hand lens because they impart a characteristic color to the soil. It is usually desirable to remove iron oxides before mineralogical analyses because of their cementing ability and masking effects. Many techniques have been devised (2, 18, 21, 33, 37, 47) to remove iron oxides. Unfortunately it is difficult to ascertain whether the treatment removes only amorphous materials.

The early researchers were primarily concerned with the removal of the iron oxides. When they found changes in the clays after the extraction, they began to realize that these amorphous materials might be important in the characterization or development of soils. There is now good evidence that soil forming processes as well as parent materials are important in the kinds and stability of the amorphous materials that occur in soils.

The more recent efforts of researchers (18, 21, 33, 47) have been towards the rapid and efficient removal of sesquioxides and the differentiation and characterization of the amorphous sesquioxides as differentiated from the crystalline sesquioxides.

Tamm (72, 73) was among the first to propose a method of removing amorphous sesquioxides from soils

as a means of distinguishing between podzols and brown earths. An acidified ammonium oxalate (referred to hereafter as oxalate) extraction procedure was used by he and Altmann in Finland to determine the rate of podzol development. Tamm's oxalate procedure was used by Lundblad (40) and by Muir (51) to separate podzols and a variety of brown earths common in Britain. According to Muir's results (51), the oxalate method did not work satisfactorily for heavy textured soils. He felt that the oxalate method's primary use was to determine the rate of soil development and to distinguish between types of soils, rather than as a method to clean up clays for mineralogical analysis.

Other researchers were more concerned with the removal of the sesquioxides, especially iron oxide. Deb (21) in studying the importance of iron oxides in podzolization, laterization and phosphate fixation compared Tamm's procedure with a procedure utilizing sodium dithionite as a reducing agent. Tamm's procedure where the extraction is done in darkness was compared with the same procedure in bright sunlight; with Deb's proposed dithionite procedure, with a sodium acetate-tartrate buffer. Deb's results showed that Tamm's procedure extracted less sesquioxides than his dithionite procedure or the sunlight

oxalate extraction. He found that the sunlight-oxalate procedure caused breakdown of silicate minerals and also encountered precipitation problems. Deb's dithionite procedure reduced the CEC of the treated clays (a measure used to determine the efficiency and completeness of removal of sesquioxides) while Tamm's procedure increased the CEC. Deb felt that the sesquioxides extracted by Tamm's procedure uncovered additional exchange sites on the clay, while his procedure, in lowering the CEC, removed amorphous as well as crystalline sesquioxides which possess some cation exchange capability or detroyed some of the clay. Deb's procedure was primarily designed for the cleaning up of clays for mineralogical studies. The measurement of the extracted iron gave an indication of the fine readily removed amorphous and crystalline sesquioxides.

Aguilera and Jackson (2) advocated the use of a sodium citrate-sodium dithionite medium for removing coatings and fine oxides before mineralogical examination. Their procedure was effective in the removal of the amorphous materials.

Gorbunov (32) when studying the solubility of minerals in soil profiles found that Tamm's oxalate procedure extracted only part of the non-silicate sesquioxides. The oxalate had some ability to attack only specific substances.

Mehra and Jackson (47) tested several methods of extraction against one proposed by them which was a sodium citrate system buffered with sodium bicarbonate and containing sodium dithionite. The sodium citrate acts as a chelating agent helping to remove some aluminum coatings and silica cements. The sodium bicarbonate kept the pH within a narrow range where there would be less problems with precipitation, as was the case with Deb's (21) sunlight-oxalate procedure, and with Aguilera and Jackson's (2) extraction procedures.

Gorbunov et al (32) in comparing all of the methods listed above as well as others, found that none of the methods removed all of the sesquioxides in one treatment. They found that Tamm's or Mehra and Jackson's methods appeared more specific for amorphous sesquioxides while Deb's was most specific for hydrated iron oxides.

Coffin (18) defined free iron to include the iron oxides and other forms of iron found in soils that are not the iron incorporated in crystal lattices of other minerals. The purpose of his study was to compare procedures using sodium dithionite as to their efficiency in iron extraction. Coffin (18) determined the effects of pH, temperature, and reagent concentrations; using the results in the development of a more efficient extraction procedure.

He used a buffered sodium citrate solution and found that a solution .15M in sodium citrate and .05M in citric acid (giving a .2M citrate concentration) when mixed with onehalf gram of sodium dithionite, gave an extracting pH of 4.75. This pH is much lower than the Mehra-Jackson extraction pH of 7.3 (47). A most interesting result of Coffin's work is the rate of removal of iron from soils. He found that a large initial amount of iron was removed within a short time period, followed by a much slower rate of removal of the remaining extractable iron oxides. He concluded that more than one form of iron oxide was removed. The extraction of iron from hematite was slower yet than the slower rate of extraction from the soil. faster rate (18) of removal from the soil was thought to be due to soil iron present in the form of coatings rather than as discrete particles. Coffin's procedure removed as much iron at a pH of 4.75, and a temperature of  $50^{\circ}$  C. in 30 minutes extraction time as the Aquilera and Jackson (2) or the Mehra and Jackson (47) procedures using a pH of 7.3 at a temperature of  $80^{\circ}$  C. and three fifteen minute extractions. All three procedures removed about the same amount of iron. The advantage of Coffin's procedure is its efficiency. Coffin reported an average standard deviation of ±.034% iron for duplicate values.

Franzmeier et al (30) in their studies of spodic horizons, considered pyrophosphate among other chelating agents. The standard against which any proposed extraction procedure was compared was Mehra and Jackson's (47). Pyrophosphate was selected because of its ability to extract organic matter and aluminum as well as iron. would also be possible to determine the amount of extractable carbon. Coffin's procedure was used except for a different extracting pH, and the substitution of .2M sodium pyrophosphate for .2M citrate (18). A pH of 7.3 was used (30) because the maximum extraction effeciency was found to occur at this point with less dissolution of silicate minerals. Their results showed that multiple extractions with pyrophosphate-dithionite and citratedithionite removed similiar amounts of iron and that one extraction of pyrophosphate-dithionite removed about 75% as much iron as multiple extractions of citratedithionite. More aluminum (30) was extracted by pyrophosphate-dithionite than citrate-dithionite regardless of the number of treatments.

Lundblad (40) used the acid ammonium oxalate procedure of Tamm (72, 73) in his studies of podzols and brown forest soils and found that the oxalate method gave a measure of the degree of recent soil weathering but not necessarily

the total weathering. Lundblad (40), like Deb (21), found a large increase in the CEC of clays after the oxalate extraction procedure, but the CEC of a podzol B horizon was decreased. He concluded that the oxalate removed the organic complexes which possessed cation exchange capacity in podzol B horizons and the clay remaining contributed the CEC left after treatment. In contrast, most investigators (2, 21, 47) using the dithionite extraction methods found that the cation exchange capacity of the clay after treatment was greatly decreased.

McKeague and Day (43) used a wide range of iron enriched horizons of Canadian soils as well as prepared amorphous and crystalline iron and aluminum oxides to compare Mehra and Jackson's citrate-dithionite (47) procedure with acid ammonium oxalate. They also tested the effects of pH, time of extraction, etc., in proposing an efficient extraction method utilizing oxalate. Extraction at a pH of 3 with a 4 hour shaking time gave the best results. Their data indicated that there was very little silica dissolution at a pH of 3. Schwertmann (66, 67) in retesting acid ammonium oxalate found that if the extraction was carried out in darkness, only amorphous oxides were removed. McKeaque and Day (43) extracted their samples

in the dark. They found that both of the procedures extracted more iron and aluminum from freshly prepared amorphous aluminum material than from silicate minerals. Much more aluminum was extracted from the freshly prepared amorphous aluminum materials with acid ammonium oxalate than with the citrate-dithionite procedure. McKeaque and Day (43) found that both treatments extracted more iron and aluminum from the solum than from C horizons. Also, oxalate extractable aluminum exceeded citrate-dithionite aluminum in most cases. They also concluded that some of the iron and aluminum dissolved by the oxalate occurs as metal-organic complexes. They also concluded that the oxalate values give an estimate of the amorphous materials formed by weathering processes regardless of the soil parent material, pH, organic matter content, or total iron The oxalate method was an especially useful indicator of the development of podzol B horizons in soils derived from parent materials high in iron content, as well as being a better extractor of aluminum.

McKeague (44) in a later report compared Franzmeier et al (13) pyrophosphate-dithionite procedure with a procedure using only .1M sodium pyrophosphate, and acid ammonium oxalate. He concluded that Franzmeier's procedure was not specific enough in extracting iron and that the

useful as the extractable carbon content. Because extractable carbon did not give any major advantage, the pyrophosphate-dithionite procedure was dropped from further consideration. The phosphorus also interfered with the aluminum determination while the excess oxalate was destroyed during the HNO3-N2SO4-HClO3 treatment used to destroy the extracted organic matter. The problem with the .lM pyrophosphate extraction procedure was obtaining clear extracts. The samples had to be centrifuged at 20,000 times gravity to produce clear solutions. The .lM pyrophosphate removed only amorphous materials from B horizions of soils.

## B. Organic Matter - Its Role in Podzolization

Tamm and Holmen (74) studied the rate of organic matter turnover in Swedish podzol soils under conifer vegetation. They found the composition of the mor humus layer to be closely related to the previous forest generation. On plots that had been cleared one hundred years ago, there was rapid loss of organic matter from the 02 horizons. The age of the podzol B horizons from the same cleared sites was only slightly younger, as

determined by C-14 dating, than the age of similar B horizons from continuously forested plots.

The surface organic layer is also important in tree nutrition, especially nitrogen. They found that about 90% of the tree's nitrogen supply comes from the surface organic layer. However, large stores of humus also occur in the B horizons of podzols. This store of organic matter becomes very important in forest regeneration after fire or clear cutting. The authors found that the organic matter was older with increasing depth as well as being slowly broken down in the B horizons.

Organic matter plays an important role in the development of spodic horizons as well as of the entire solum.

Non-humic substances (23) appear to have more evident structural characteristics. Included are carbohydrates, proteins, waxes, lignin, etc., and partially decomposed plant and animal tissues. Most of these materials are readily attacked by soil micro-organisms and have a rapid turnover rate.

Humic substances are those organic compounds that are generally amorphous and relatively resistant to further chemical breakdown. They are generally yellow, brown, or black, acidic substances of relatively high molecular weight (23). Based on solubilities, there are

three components: fulvic acid, humic acid, and humin (28). Fulvic acid substances have the lowest molecular weight, and are soluble in both dilute acid and alkali. The humic acid substances are soluble in alkali but insoluble in acid. Humin substances are generally insoluble except when extreme measures are taken.

Various extractants of soil organic matter have been tested (20, 27, 28, 56, 75). Felbeck (28) has recently reviewed the chemistry of soil humic substances. NaOH extracts the greatest amount of organic matter but problems of hydrolysis and auto-oxidation are involved in its action. Neutral salt solutions and acids have also been used. The color of the extracting solution is not a good index of solubility since NaOH extracts, although lighter in color, contain more dissolved organic matter than darker colored pyrophosphate extracts.

How well a particular extractant works depends upon the kind of soil and the soil horizon. Organic matter in podzol B horizon is soluble in several reagents (61).

The type and composition of the extracted organic matter depends upon the extractant, the pH, the time of shaking, and other variables that effect the extraction (28).

NaOH and NaCO<sub>3</sub> are widely used as alkali types of extractants (28). Fulvic and humic acids are made soluble with these extractants. The solubility of organic matter in alkali is due to the ionization of the acidic components.

Felbeck (28) points out that most soil organic matter is quite insoluble in dilute acids but more soluble than in water. Acids cause the hydrolysis of organic matter which involve the splitting of the organic molecule and the addition of H and OH groups from water. Felbeck concludes that acid hydrolysis was effective for the non-humic organic fraction but had little effect on the humic acid fraction.

Coffin and Long (17) showed that humic acid extracts from a podzol Bh horizon contained phenols and phenolic acids as well as dihydroxybenzoic acids. They found that these substances accounted for about 12% of the soil organic matter. Lignin and the products of lignin decomposition make up a large percentage of the humic acid component. Schnitzer et al (6) have found the organic matter of a podzol B horizon to be soluble in both dilute acid and alkali. Barton and Schnitzer (10) found that 90% of the organic matter extracted from a podzol Bh horizon was completely soluble in dilute acid and alkali.

Several hypothesis (28) to account for these properties have many features in common. The humic substances are believed to be amorphous, three dimensional, polymeric, acidic, organic materials that have a high molecular weight with an aromatic type of structure.

Several organic solvents have been used (20, 63) to extract organic matter from podzol B horizons. The organic solvents acting as chelating agents, are able to extract organic matter from these horizons but in other soils, organic chelating agents are not effective extractors of organic matter (63).

Schnitzer and Wright (6) experimented with the organic matter from the Ao and Bh horizons of a Canadian podzol in order to determine the chemical components and to show the role that organic matter had in podzol development. They used an alkaline permanganate oxidation procedure and a nitric acid oxidation procedure in an attempt to characterize the organic matter from the above mentioned horizons. They report that with the permanganate oxidation, the organic matter in the Ao horizons had twice as many steam volatile acids as the Bh horizons. They concluded from their studies that using the procedures described above, the organic matter in the Ao horizons

had appreciable amounts of aliphatic and/or alicyclic along with aromatic organic structures. The organic matter from the Bh horizons had primarily aromatic structures. Wright and Schnitzer (8) found that the fulvic to humic acid ratios of alkali extracted organic matter from these Ao and Bh horizons were .4 and 5.6, respectively. They concluded that fulvic acid played a prominent role in the metallo-organic reactions associated with podzolization. The Bh horizon content of fulvic acid accounted for 85% of the total organic matter. Alexandrova (3) studied organo-metallic complexes in soil organic matter. He recommended that to isolate the aluminum and iron organic complexes sodium pyrophosphate at a pH of 8-8.5 be used. He found that the organo-metallic complexes accounted for 30-40% of the soil humus in podzol B horizons.

Whitehead et al (80) using an organic solvent dimethylformamide extracted soil organic matter and found
that aluminum and silica were the largest inorganic contaminants. Umesh et al (75) used Schweitzer's reagent to
extract cellulose from soil organic matter. The isolated
cellulose comprised .3 to 1.9% of the total organic
matter in the soils they studied. The percentage of
cellulose was higher in podzolic soil organic matter and
lowest in brown forest soils.

Yaun (83) compared reagents used to extract soil organic matter. He found that NaOH, Na4P2O7, NaF, 7

Dowex A-1 in their ability to extract organic matter from surface soil horizons. The extracting ability of the same reagents for a Leon organic-iron pan was NaOH, NaF, Na4P2O7, Dowex A-1. Schnitzer et al (63) found that as more metal (Iron and aluminum) was complexed by organic matter extracts, that the water solubility of the material decreased. They extracted the Bh horizon of an Armadale soil with dilute HCl and found that the extract had similar complexing ability to laboratory prepared metallo-organic substances.

Duchafour (24) found that the fulvic acids were abundant in acid soil humus while humic acids predominated in podzol B horizons. However, Fe complexed by fulvic acid was mobile and also occurred in relatively large amounts in the podzol B horizon. The Fe complexed by humic acids was insoluble. Wright and Schnitzer (81) found that fulvic acids comprised most of the podzol B organic matter fraction. So, there is some disagreement. This may well be due to the extraction procedures that were used, but isn't it also likely there are a number of kinds of podzolic B horizons that may differ in properties and genesis?

Wright and Schnitzer (82) leached a calcareous parent material with EDTA. After a period of leaching, the soil column had the appearance of a podzolic profile except for an O2 and Al horizon which were missing. found that iron and aluminum were mobilized, transported and redeposited. They postulate that under natural conditions fulvic acid is the agent responsible for the translocation of iron and aluminum in the podzolization process. Fulvic acid with a dominantly aromatic structure forms water soluble chelates of iron and aluminum. precipitation at lower depths may be caused by an over abundance of iron and aluminum and/or by very small amounts of calcium and magnesium ions. Adachi (1) used B horizon soil material from a volcanic-ash and a red-yellow soil and leached them with fulvic acid. He found that at first, all of the fulvic acid was absorbed by the soil. Then. aluminum began to be eluviated followed by iron. mobolized aluminum and iron were precipitated in a lower position due to a change in the sesquioxide/fulvic acid ratio. Later, silica and sesquioxides were aluviated more intensely.

Posner (56) tested the ability of NaOH,  $Na_2P_2O_7$  and  $Na(CO_3/HCO_3)$  to extract humic acids from a soil. He

found that at room temperature  $Na_2P_2O_7$  produced humic acids with the lowest ash content. The iron content of the humic acids extracted did not correlate with their silica or aluminum contents. Evans (27) tested several extractants at various pH levels in order to find the best combination of extractant and pH for optimum extraction ability. He reported that organic matter extraction with NaOH and  $Na(CO_3/HCO_3)$  extractants does not become significant until the pH is above 8.5, and that above pH 10.5 the extraction becomes very rapid. Pyrophosphate also responded to pH in the same manner. The results showed that the pyrophosphate extracts contained less fulvic acid than the alkali extracts. Evans states that the presence of iron and aluminum in the extracts was no proof of their association with the soil organic matter.

Schnitzer (60) studied the effects of the leachate from freshly fallen leaf litter on the mobilization of sesquioxides in podzols. He found certain similarities between soil organic matter and the fresh leachates in composition and in complexing ability with iron and aluminum. Many researchers (11, 12, 38, 60) have studied the effects of leaf leachates on sesquioxide mobility. Coulson et al (19) found that iron was mobilized by the

polyphenol leachate component at low pH. They found that the movement of aluminum was dependent on pH, not on the type of leachate. The precipitation of iron polyphenols (normallywater soluble) was thought to be brought about by microbial activity. Martin et al (41, 42) studied the effect of various metals commonly found in podzolic soils when in contact with humus extracts. They found that there was a critical pH of precipitation. below which there was complete solubility and above which there was peptization and solubility. The critical pH for iron-humus compounds was 2-3. These pH values are very close to the pH of precipitation of hydrated aluminum and ferric hydroxides, respectively. At a pH of 5 partial precipitation also occurred. The writers suggest that the aluminum ion as well as the magnesium and calcium ions may be responsible for the flocculation of humus in the upper B horizon of podzol soils.

Schnitzer and Gupta (62) characterized the organic matter of a Gray Wooded soil from Canada. The experimental data showed that the humic and fulvic acids were similar to podzol humic and fulvic acids. The Gray Wooded organic matter had a larger amount of phenolic hydroxyl groups. In analogy to podzols, 70% of the organic matter

extracted from the Gray Wooded O horizon consisted of humic acid, while 90% of the organic matter from the Gray Wooded B2 horizon was fulvic acid. The organic matter was difficult to extract because of its close association with the clay. The two major differences between podzol and gray wooded organic matter was that less organic matter was extracted from the Gray Wooded soil and the close association with clay. The vegetation under which the Gray Wooded soil was developing was Populus tremuloides.

Bloomfield (11) used aspen and ash leaf leachates to determine the effects on iron and aluminum mobilization. He found that both types of leaves were able to mobilize iron and aluminum at high pH (pH 7) thus enabling the development of spodic horizons in high pH soils developing from calcareous parent material. The leaf leachates also contained appreciable amounts of calcium No podzols have been found to occur under ash compounds. It was thought that earthworm activity, vegetation. being much greater under ash forest, churns the upper horizons masking the effects of podzolization. (48) also studied the composition of leaves associated with varying degrees of podzol development for the effect they may have on podzol formation, and reviewed the literature pertaining to leaf leachates, mor and mull humus research.

## C. Methods of Aluminum Analysis

Most methods for determining aluminum rely on the formation of a colored reactant. The major requirement for accurate and reproducible measurement is to have only aluminum ions in the solution (46). However, this rarely occurs. In the absence of interfering ions, many methods to determine aluminum can be used (46). Besides the colorimetric methods which are in common use, titration and gravimetric methods are also used. Gravimetric methods (46) are subject to all the disadvantages of colorimetric methods plus some additional ones.

The "aluminon" method is commonly used for routine aluminum determinations. It is fairly reliable provided the procedures used are closely followed. The solution to be analyzed must have a certain pH, have low concentrations of interfering ions, etc. Jackson (36) gives the procedures which are necessary in most cases so that the aluminum content can be determined. Research (46) results show an inherent error for the procedure of ±3%. Many ions interfere. Among these are iron, calcium, phosphate, and oxalate. The usual way to control interfering ions is to remove them by precipitation processes or by adding inhibitors (36, 46).

Another method for determination of aluminum which is gaining favor because of its rapidity and precision is atomic absorption spectroscopy. Prince (57) covers the principles and methods of atomic absorption spectroscopy. Recent developments in techniques (39, 55) have made possible the accurate determination of aluminum by this method. The use of the nitrous oxide-acetylene flame, plus a special burner head, has resulted in a flame temperature hot enough to decompose most aluminum compounds and to excite the aluminum ion.

Pawluk (55) using a Perkin-Elmer 303 stated that the accuracy and precision were similar for ion exchange or total elemental analysis provided that standard solutions were prepared in the same manner used to prepare the unknown samples. This is especially important in aluminum analysis. Pawluk conducted aluminum analysis on a Perkin-Elmer 303 modified to determine aluminum using standard procedures outlined in the analytical procedures manual (7). The following shows his comparisons between Al. determinations by atomic absorption and by an accepted gravimetric method (55).

Comparison of Aluminum Determination Methods by Pawluk. Total Aluminum Content

<u>Sample</u>	Atomic Absorption	<u>Gravimetric</u>	
Bytownite Albite	32.5%	32.55%	
Microcline	20.31 20.40	20.27 20.20	
Rock 1 Rock 2	17.34 31.27	17.21 31.28	
Na-feldspar	18.95	19.06	

Recovery tests indicated that there was complete recovery of aluminum added to unknowns (55). Calcium and magnesium caused no interference, but excessive amounts of sodium and potassium increased the absorption.

LaFlamme (39) used a Perkin-Elmer 303 with the nitrous oxide modifications to determine the amount of extractable aluminum in 1N KC1 and 1N ammonium acetate extractions. A precipitation was necessary to remove the excess salts from the KC1 extractions but heating destroyed the excess ammonium acetate. He found that aluminum recovery was incomplete without the addition of iron to the samples. Levels of from 40 to 100 ppm of iron were necessary for complete aluminum recovery. He ran recovery tests by adding known amounts of aluminum to unknowns. He found that there was complete recovery of all the added aluminum. LaFlamme concludes that the proposed method for determining aluminum in soils is precise, rapid and very useful, especially when many determinations are necessary.

#### 1. The Present Study

The large number of samples and the replications that would be required made it desirable to find an easier method of determining aluminum than the "aluminon" procedure. With a new modification of the Perkin-Elmer 303 (9) which made possible the rapid, accurate determination of aluminum, a study was conducted by Gary Steinhardt (70) and the author to study any interferences and measure recovery of aluminum with the extracting agents commonly used to remove amorphous materials from soils. Steinhardt (70) tested for interferences and used procedures necessary in some cases to remove interfering ions.

Steinhardt working with aluminum standards added to a known amount of aluminum 5 and 200 ppm of boron, calcium, copper, magnesium, manganese, molybdenum, phosphate ion, silicon, sulphate ion, and zinc. The results showed a positive interference in percent absorption from 200 ppm of calcium, phosphate ion, and silicon of about 10-16% and a negative interference for 200 ppm of the sulphate ion of about 5%. The results from the addition of 5 ppm of the various ions showed no interference.

Of the three extracting procedures used in this study, the acid ammonium oxalate residues were easily removed in

the organic matter destruction procedure. The excess sodium ions from the citrate-dithionite extraction, even greatly diluted, caused a 2-3% increase in absorption. The aluminum precipitation procedure that was used to rid the solutions of sodium did not give complete recovery. This was probably due to traces of the citrate ion remaining after the organic matter destruction procedure. The results from the precipitation procedure were consistently 10% lower than was expected. Steinhardt (70) attempted to precipitate aluminum and iron from a sodium citrate solution with no results, the aluminum and iron citrate complex was soluble at high pH. The Al. in the pyrophosphate-dithionite extracted samples could not be precipitated with complete recovery due to the pyrophosphate remaining even after an acid heating treatment to remove the organic matter.

In order to have good results with the aluminum analysis with citrate-dithionite and pyrophosphate extracted samples it is necessary to treat the standards exactly the same as the unknown samples. The salt content must also be kept low in order to prevent fouling of the burner head.

In conclusion, the analysis of aluminum on the Perkin-Elmer 303 is rapid, as precise as the aluminon method, requires less work, and there is less error due to the operator. The machine is very sensitive to adjustment. The greatest sensitivity from experimental work is 0.5 ppm percent absorption, from 0 to 40 ppm aluminum. The standard curve is quite straight on semi-log paper. A great advantage was the ease of rechecking samples as well as the number of samples that could be run per hour.

#### D. Methods of Iron Determination

There are numerous methods for determining the iron content of soils. Olson (54) describes gravimetric, volumetric, and colorimetric methods. Jackson (36) describes the standard procedure for iron, utilizing a color reaction of ferrous iron with orthophenanthroline. All the iron must be in a ferrous state. This is done by the use of Hydroxylamine.

Hsu (34) refined an anlytical procedure utilizing thiocyanate. The thiocyanate procedure had fallen into disrepute in recent years because of difficulties with color formation, fading and interferences. Hsu used hydrogen peroxide to produce stable colors. He also tested the modified procedure for interferences, changes in concentrations, pH, temperature, and time of reading in

order to have maximum color intensity. He found that if the color faded that one drop of hydrogen perioxide was sufficient to bring back full intensity. He found that phosphate ion levels over 50 ppm caused considerable interference. No other ions tested (Al, Si, Ca) caused any interference at concentrations up to 500 ppm.

A more recent development in the search for a more rapid analytical procedure with as great or greater accuracy is the adoption of atomic spectroscopy methods. The Perkin-Elmer 303 (7) has a sensitivity to iron of .3 ppm Fe per percent absorption and as little as .05 ppm Fe can be accurately detected.

Pawluk (55) tested the determination of iron by atomic absorption methods and compared the results with those obtained by the accepted colorimetric procedure utilizing o-phenanthroline. His results were as follows:

Comparison of Methods of Iron Determination by Pawluk

Total	Iron	as	%Fe <sub>2</sub>	03
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<u>Sample</u>	Atomic Absorption	Colorimetric
clay 1	7.05	6.90
clay 2	7.49	7.45
clay 3	7.80	7.86
clay 4	3.60	3.68
clay 5	3.60	3.68
soil 1	2.94	2.94
soil 2	2.88	2.86

In another comparison, the extractable iron content with a citrate-dithionite extraction method was compared using atomic absorption and o-phenanthroline. Atomic absorption measurements were made before and after treatment to remove sulphur, excess dithionite and citrate and organic matter. There were no differences in the results. Organic compounds do not cause interference. The results obtained by the two procedures were in close agreement. Pawluk found that the reproducibility of results were better with atomic absorption than with the colorimetric method. The advantages of atomic absorption are: rapidity, accuracy, ease of rechecking samples, few interferences, and efficiency.

## E. Methods of Determining Organic Carbon

Organic matter, as discussed earlier, plays an important role in soil development and use, especially in Spodosols. The organic fraction of the soil consists of plant and animal remains in all stages of decomposition. After decomposition has progressed to the point where no plant or animal tissues are recognizable the remaining organic matter is commonly known as humus. Humus is highly altered organic matter (6) that is quite resistent to further

chemical or microbiological breakdown. The average age of the humus in a Bhir horizon of a northern Michigan Munising soil has been reported to be 870<sup>±</sup> 110 years by the Radiocarbon Laboratory at the University of Michigan.\* Other dates (68) of organic matter in surface soil horizons from Iowa and North Dakota revealed ages of organic matter to be from 100 to over 400 years. reported radiocarbon dates of humus on spodic horizons (68) vary from 900 to 1,100 years. These dates indicate that the humus, especially the humus of subsurface horizons, is very resistant to further decomposition. The younger ages of the organic matter in the surface horizons indicate the relative rate of humus turnover in surface compared to subsurface horizons. Tamm and Holmen (74) found the age of organic matter to increase with increasing depth in podzol profiles in Sweden. found the C-14 age of B horizons in southern Sweden to be 330 to  $465^{+}_{-}$  65 years and 460 to  $1260^{+}_{-}$  60 years in Northern Sweden, while the age of organic matter in Al and A2 horizons was not much older than the present forest age.

<sup>\*</sup>Sample collected by Franzmeier, Whiteside, Johnson, Lietzke and submitted for analysis by the Geology Department at Michigan State University.

Organic matter can also occur as elemental or nearly elemental carbon (6) in soils containing charcoal as the result of fires, or as coal or graphite from sedimentary parent materials, or in cinders and ashes applied to the land. Because of the many forms of organic matter in various stages of decomposition in soils, it is difficult to quantitatively measure the amount of soil organic matter.

There are two general methods by which the carbon content of soils can be measured: the wet combustion method which uses an acid or combination of acids to decompose the organic matter, and the dry combustion method where the carbon is oxidized to CO<sub>2</sub> by the application of heat.

The wet combustion method uses strong acids to decompose or digest the organic matter and oxidize the carbon to CO<sub>2</sub>. The reaction is speeded by the reaction heat or by the application of external heat. The wet combustion method is now a common standard for routine determination of carbon in soils (6). The main advantage of the wet combustion methods (6) is the low apparatus cost compared to the dry combustion apparatus. The second advantage is that less time is required per sample. There are many procedures (6, 45, 65, 78) utilizing wet combustion.

Allison's (4) procedure has been refined from several earlier methods. His method uses a mixture of sulphuric and phosphoric acids to digest the sample. CO<sub>2</sub> free air is passed over the sample during the digestion period. The combustion gases are passed through a series of scrubbers to remove moisture, SO<sub>2</sub>, and other gases that would interfere with the results. The CO<sub>2</sub> is then absorbed on a suitable reagent and the amount of carbon determined by weighing. A time period of from 15-25 minutes is required per sample. Anderson (8) modified Allison's procedure by not using sulphuric acid, and only used phosphoric acid. He reported higher recovery values.

Other wet combustion methods utilize the reduction of the  $Cr_2O_7$  ion by organic matter. The amount of carbon consumed is determined by the amount of the chromic ion remaining. The carbon that is measured by this procedure is known as the readily oxidizable carbon content of a soil (5).

There are two rapid titration methods in use where the soil is digested in a known excess of chromic acid. Schollenbergers (64, 65) method involves the use of external heat to speed up the reaction. Walkley and Black (77) and Walkley (78) modified this type of procedure by not using external heat. These procedures do not completely

oxidize all of the carbon in the soil so correction factors are necessary (5). Walkley and Black (77) state that their procedure is accurate to within ± 5% of the carbon present.

El Attar et al (25) tested the conversion factor used in the chromic acid digestion method (1 ml of 1 N  $K_2Cr_2O_7$  equals 3 mg carbon). They found that the conversion factor varied according to the material being analyzed. The conversion factor was obtained by comparing the carbon values from the chromic acid digestion procedure with dry combustion values, which are considered the most accurate. They found that 1 ml of 1 N  $K_2Cr_2O_7$  equals 2.80 mg carbon for soils, 3.05 for humic acids and 3.62 for fulvic acids.

Bremner et al (14) compared Tinsley's method, which requires no correction factor, with Shaw's method, Walkley and Black's method and dry combustion. All of the first three methods are based on the chromic acid digestion of organic matter, but with slight modifications from each other. They found that Shaw's method closely approximated the dry combustion values. The Tinsley method values averaged 96.3% of the dry combustion values, while the Walkley-Black values ranged from 73-119% of the dry combustion values and a correction factor had to be used. The other methods did not use a correction factor.

Dry combustion methods must be able to completely oxidize and remove all carbon compounds including charcoal and carbonates if present. Two types of dry combustion furnaces: the resistance and the induction type, are used to heat the sample. The resistance type of furnace is capable of reaching temperatures of 900-1,000 C.. The high temperature induction furnace operates at temperatures of 1,400-1,600 C.

The usual method of determining the carbon content of a sample by the dry combustion procedure is by gravimetrically weighing the CO<sub>2</sub> produced after it is absorbed on Ascarite (6). With this method the sample is ignited in the presence of pure oxygen. The resulting combustion gases are purified and any interfering gases, especially moisture and sulphur dioxide, which would give a positive interference are removed.

Young and Lindbeck (84) working with a Fisher high temperature induction furnace reported on the problems that they encountered with this type of furnace in carbon analysis of soils and other organic materials. They found that during the pre-burn cycle, the products of pyrolysis or other volatile materials were commonly lost. With modifications they were able to achieve nearly complete recovery values from organic materials that contained a

known amount of carbon. Stewart et al (71) using a Micro-Dumas method with a Coleman Nitrogeo Analyzer, Model 29, found that the recovery values of organic carbon compounds as well as soils ranged from 98 to 101%. They also compared the results with other procedures (71) and found that the results from the above analyzer compared very favorably with the other methods. They found that the average relative standard deviation from the mean for soils was  $\pm 2.24\%$  of the mean value. The Leco Corporation has a carbon analyzer that uses a high temperature induction furnace plus a new method of determining the carbon content of a sample. The analyzer was originally designed to determine the carbon content of steels and iron but several researchers have been investigating its use for determining the carbon content of soil samples. Arshad and Lowe (9) reported that the total amount of organic carbon as determined on a Leco analyzer compared very favorably with Allison's wet combustion method. Only the results that were determined on the Leco analyzer are reported in the paper.

# 1. The Present Study

Many problems must be surmounted in the development of an accurate routine method for determining the carbon

content of soils. One major problem is the very small sample that must be used, from 100-500 mg for most procedures. In order to insure a representative sample, the soil must be ground very fine. The mortar and pestle is the most common but hardest and most time consuming way to reduce the sample particle size without the loss of carbonaceous dust.

A Leco carbon analyzer, Model 598-500, with digital readout, designed for the determination of carbon in iron and steel samples was purchased by the Soil Science department at Michigan State University in 1967, after some preliminary work showed that it had possibilities for determining the carbon content of soils. Gary Gascho (personal communication) conducted the initial tests. He found that optimum sample size for soil samples was between .1 and .2 grams. It was necessary to raise the pre-burn temperature in order to have complete combustion during the burn cycle. A larger amount of iron chip was added to the samples in order to compensate for their low iron content. E. C. Doll (personal communication) reports that there are some unexplained differences between Leco values and the usual dry combustion method values.

In this study, both oven dry and air dry samples were analyzed. There were no detectable differences in the results. The anhydrone moisture trap needed to be changed every 10-15 samples when air dry samples were analyzed. Thirty or more oven dry samples could be analyzed before the moisture trap needed renewing. If the anhydrone in the moisture trape became wet to a depth greater than 1/4-1/2 inch, there was danger of moisture in the combustion gases passing on through into the collection chamber, increasing the carbon value reported. Only two explosions occurred and those were when igniting organic surface horizons (0<sub>2</sub>) that were not completely air dry.

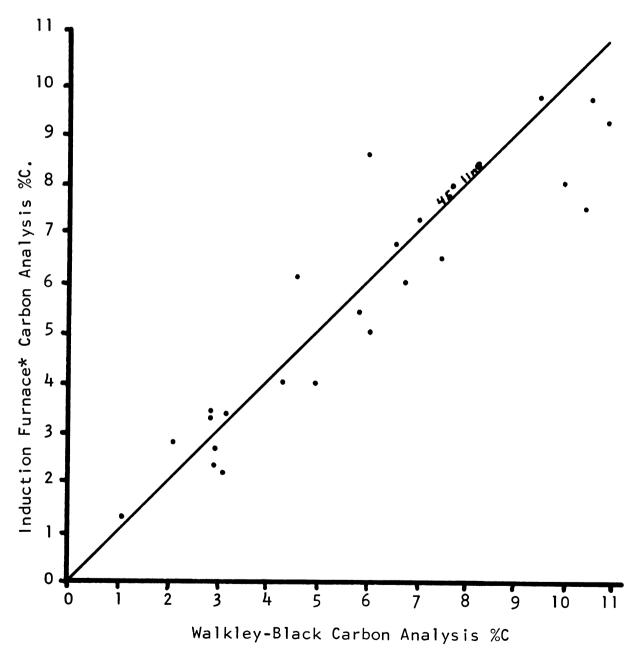
Over 100 samples were analyzed. All were from naturally wooded or uncultivated areas. All samples contained no free carbonates. The samples consisted of surface and subsurface horizons of Spodosols and soils closely approaching Spodosols from northern Michigan. With a 2 minute cycle per sample, it was easy to run many replicates. From 2-4 replications were made on each sample. The average values are shown in Table 13, along with the Walkley-Black

values reported by the SCS Beltsville laboratory, for each horizon. An analysis of variances within and between the two methods was run. In this analysis the surface horizons, the A2, the B21, the B22, etc., were each grouped together. F ratios obtained showed no significant differences between methods on the surface horizons, but highly significant differences occurred for all of the other horizons in the comparison of methods.

Figure 1 shows the values from the two methods plotted against each other for all of the surface horizons. The values are about evenly distributed on each side of the mean 45° line, with only a few values falling outside a range of 1% difference in carbon content paired values, or 16.6% of a mean determination. Figure 2 shows the carbon values from the two methods plotted against each other for all of the subsurface horizons. In this graph all of the Leco carbon values exceeded the Walkley-Black values except three, with an average difference of +0.2% in carbon content between the methods, or +25% of a mean determination.

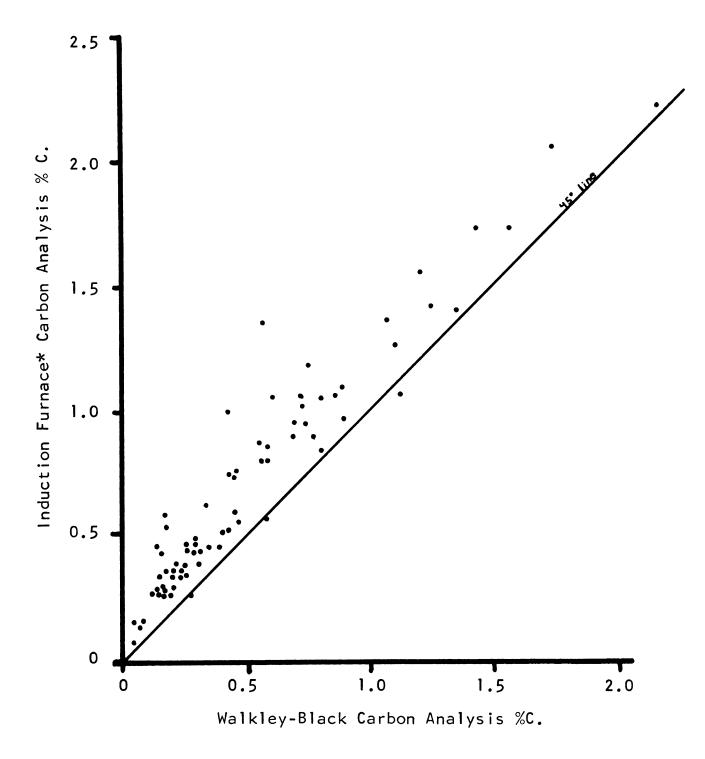
Computer analysis of the Leco carbon determinations showed that there was an average coefficient of variation (C.V.) of 12.08%. When the C.V. was plotted against the mean carbon value for corresponding sets of values, there was a trend to increasing C.V. with decreasing carbon content

Figure 1. Comparison of Carbon Determinations; Induction Furnace vs Walkley-Black, for Surface Horizons



\*Leco Carbon Analyzer

Figure 2. Comparison of Carbon Determinations; Induction Furnace\* vs Walkley-Black for Subsurface Horizons.



\*Leco Carbon Analyzer

of the sample, for the subsurface horizons. The surface horizons showed a trend of the opposite nature, that the C.V. tended to increase with increasing carbon content. Soil texture also resulted in differences in coefficients of variation. Sand textured soils low in organic matter had much higher C.V. than sand soils that had relatively high organic matter contents or soils with textures finer than sand. The Grayling, Kalkaska and Omega soils had much higher C.V. than the average. A2 horizons and horizons below the spodic horizon also had much higher C.V. than the The soil samples having textures of sandy loam to loam had an average C.V. of 8.89% for all horizons and an average C.V. for the spodic horizons of 5.14%. The sand soil samples had an average C.V. of about 12.43% for all horizons and an average C.V. of 9.80% for the spodic horizons.

Undoubtedly, the major source of error in the carbon determination is in the sampling. With the small sample size, fine grinding is necessary particularly in surface horizons where organic fibers are common. But even with a fine particle size, there is a large difference in density between the organic particles and the mineral grains. It was nearly impossible to mix a sample, then take a small subsample out and not see lighter and darker colored streaks, a sure indication of lack of homogeneity. One method of

overcoming the poor mixing would be to determine the average carbon contents of at least 3 or 4 samples from one horizon. In this way the error due to sampling shouldn't be as great. A piece of tiny rootlet in a sample low in organic matter can cause a large variation. This is probably the main reason for the large C.V. of A2 horizons, and horizons below the spodic horizons. Probably half of the C.V. can be attributed to poor sampling, some can be attributed to the carbon content of the sample and some to the texture of the sample. All three interact with each other to either add to the error or to tend to subtract from the error.

## F. Extraction Procedures

1. Pyrophosphate-Dithionite (Franzmeier et al (30, 31))

Place 3.8 grams of air dry soil (fine earth fraction) into a 100 ml plastic centrifuge tube. Mix 76 ml of 0.2M sodium pyrophosphate solution with 1.9 grams of dry sodium dithionite in a 100 ml beaker. Stir immediately to dissolve or else a hard deposit from the chemical reaction occurs which is difficult to dissolve and add to the sample in the centrifuge tube. Heat the unstoppered tubes in a 50°C. water bath. After a 10 minute heating period, stopper the tubes and shake. Shake again every 5 minutes at the 5, 10, 15, 20 and 25 minute intervals. Shake the tubes in a uniform manner. At the end of the 30 minute extraction

period, centrifuge the samples at 2,000 rpm or at whatever rpm is necessary in order to have clear extracts. Immediately remove a 5 ml aliquot for iron and aluminum determination and a 50 ml aliquot for extractable carbon determination if desired.

#### Digestion Procedure

To a 50 ml beaker containing the 5 ml aliquot, add from 1 to 5 ml of a strong acid mixture containing acids in a ratio of 10 parts HNO3, 4 parts H<sub>2</sub>SO<sub>4</sub> and 4 parts HC1O<sub>4</sub>. Cover the beaker with a watch glass and heat on a hot plate until taken to dryness. After cooling, add 0.3 N HC1 to dissolve the residues. The extract should be clear and colorless at this point. The extract should be diluted to a known quantity. The dilution depends on the iron and aluminum content of the sample.

## Preparation of 0.2M Sodium Pyrophosphate

The solution is prepared by weighing out 89.2 grams of sodium pyrophosphate ( $Na_4P_2O_7\cdot 10\ H_2O$ ) per liter or multiples thereof. The pH is adjusted to a value of 8 by adding hydrogen saturated cation exchange resin. After pH adjustment, the resin is removed by decantation and filtering. Care must be taken not to spill or otherwise lose any solution. A final dilution is made to bring the solution up to the final volume.

Proper selection of an acid to hydrogen saturate the resin must be considered. Some anions interfere with colorimetric methods of determining iron and aluminum. No anions other than phosphorus caused interference with atomic absorption determination of iron and aluminum.

Iron and Aluminum Determinations

#### <u>lron</u>

In this study all iron and aluminum were determined by atomic absorption on a Perkin-Elmer 303. A dilution factor of 2/100 for iron determination was found to be necessary for many citrate-dithionite samples in this study. Some samples required further dilution. A dilution factor of 5/50 was necessary for the ammonium oxalate extracts, and a dilution factor of 5/100 was necessary for the pyrophosphate-dithionite extracts.

#### Aluminum

As it was necessary to add additional iron to the extracts in order to determine aluminum, iron determinations were done first. With the oxalate samples, a 20 ml aliquot was placed in a 25 ml volumetric, enough iron was added to increase the sample iron content to 40-100 ppm, and the volume make up to 25 ml. It is necessary to add additional

iron to the citrate-dithionite samples in the same manner as with the oxalate samples. However the aluminum standards must contain the same amount of iron and sodium citrate and be treated in the same manner as the extracts in order not to have any interferences. The pyrophosphate samples must have iron added also and the standards must have the same concentration of sodium pyrophosphate and iron and be run through the organic matter destruction procedure in the same way as the samples, in order to negate interferences.

## 2. Ammonium Oxalate (McKeague and Day (43))

An accurately weighed sample of between 150 and 400 mg. depending on the iron content is placed into a 15 or 20 ml plastic centrifuge tube. 10 ml of acidified ammonium oxalate is carefully pipetted into the tube. The tubes are stoppered tightly and placed horizontally in a light tight container. The container is placed on a reciprocating shaker for a 4 hour shaking period. After shaking, the tubes are centrifuged for 5 minutes at 2,000 rpm or whatever rate is necessary to have clear extracts. A 5 ml aliquot is carefully removed and placed in a 50 ml beaker. Iron and aluminum determinations are then as given above.

#### Preparation of 0.2M Acid ammonium Oxalate

The solution is prepared by mixing together 0.2M solutions of ammonium oxalate and oxalic acid until a pH of 3 is obtained. The oxalic acid is poured into the ammonium oxalate. The resulting solution is 0.2 M with respect to the oxalate concentration.

## 3. Citrate-Dithionite (Mehra and Jackson (47))

Four grams of air dry soil is put into a 100 ml centrifuge tube. 40 ml of 0.3 M sodium citrate solution is added along with 5 ml of 1 M sodium bicarbonate solution. The tubes are placed in an 80°C, water bath. When the solution temperature reaches 80°C., 1 gram of solid sodium dithionite is rapidly added while stirring the solution continuously until complete mixing is achieved. The samples are stirred occasionally during the 15 minute extraction period. Care must be taken to treat all samples the same with respect to the amount of stirring that is done. not let the water bath temperature exceed 80°C.. After the 15 minute extraction period, 10 ml of a saturated sodium chloride solution is added to flocculate the clay. samples are centrifuged in order to have clear extracts. The digestion procedure and iron and aluminum determination methods are as stated above.

Note: All values reported in this paper are based on soil in air dry condition. It was felt that undesirable conditions might result or changes occur if the soil samples were oven dried. An analysis of the difference between air dry and oven dry weights on 35 samples averaged 0.77% and ranged from 3.66% in 02 horizons, to 0.08% in sand C horizons. The difference between the air dry and oven dry conditions was judged to be insignificant for purposes of this study.

# 4. Discussion of Extraction Procedures Ammonium Oxalate Extraction Procedure

McKeague and Day (43) and McKeague (44) retested the acid ammonium oxalate extraction procedure of Tamm (72, 73) as a means of differentiating various classes of soils in Canada. They compared the ammonium oxalate extraction carried out in darkness with Mehra and Jackson's (47) citrate-dithionite extraction procedure, Franzmeier's (30) pyrophosphate-dithionite procedure and Bascomb's (44) 0.1M pyrophosphate extraction.

When comparing the oxalate with the citrate-dithionite method, McKeague and Day found that the oxalate method

extracted very little iron from 100 mesh goethite or hematite while the citrate-dithionite method extracted a large quantity of iron from these minerals. In a comparison of the two methods abilities to extract aluminum from amorphous aluminum silicates, McKeague and Day found that the oxalate procedure extracted much more aluminum than the citrate-dithionite procedure.

In further tests using soils, McKeague and Day found that 15 out of 50 soil samples had greater amounts of extractable aluminum than iron when extracted with ammonium oxalate, and only 7 of the 50 had greater aluminum than iron when extracted by the citrate-dithionite procedure. They concluded, from their data and data from earlier experiments, that some of the aluminum and iron extracted from Podzol B horizons existed as metal-organic complexes, and that more aluminum occurred as inorganic than organic complexes. McKeaque and Day concluded that both the oxalate extractable iron and aluminum as well as the citratedithionite extractable iron and aluminum values aided in the distinction of Podzols from other soils as well as distinguishing between the various classes recognized within Podzols. They found that all Podzol B horizons had distinct accumulations of oxalate extractable aluminum.

They also concluded that the oxalate values gave a better indication of the amount of accumulation of amorphous materials which are the result of recent weathering processes (since deglaciation). The oxalate iron values also gave a better indication of Podzol B development in soils derived from reddish parent materials high in iron content. The citrate-dithionite method could not differentiate between the products of recent weathering and fine crystalline iron particles. McKeague and Day also found that the oxalate iron and aluminum values were associated with horizons having a high pH dependent cation exchange capacity and high phosphorus fixing ability.

The method of McKeague and Day utilizing an acid ammonium oxalate extraction procedure was used to extract the soils used in this study with the thought of finding out how Michigan Spodosols compared with their Canadian counterparts.

The oxalate extraction procedure was by far the easiest and most efficient of the three methods that were evaluated. The actual number of samples that could be extracted per day was nearly the same as with the citrate-dithionite procedure, but during the 4 hour shaking period, other work could be done. The necessity of an accurate average

subsample and accurate weighing to three decimal places is important in achieving a representative average value, or reproducible results.

Usually, when grinding such small samples (100-400 mg) it is necessary to grind a much larger sample to pass through a 100 mesh sieve. However in the grinding process, iron contamination and the loss of fine clay and carbonaceous dust occurs with a lowering of the resultant values. No sample grinding was done for any of the extraction procedures except for the carbon determination. In this case the samples were ground by hand with a mortar and pestle. Even with this type of grinding, care was required not to have dust flying away. After sieving and mixing the large samples, a "representative" subsample was withdrawn and served as the sample source for the laboratory analysis of iron, aluminum, and carbon.

Forty-eight samples, representing primarily B horizons were replicated 2 to 4 times in order to check the reproducibility of the extraction procedure. The computer analysis of the data revealed that the average coefficient of variation for the iron determination was 13.90%. Included in this C.V. is the sampling, weighing, slight differences in moisture content, errors in pipetting, and the machine error in analyzing the samples for iron. The major source of error is in obtaining a sample that represents

an accurate average of the horizon as it occurs in the field. The error in the extraction procedure and analysis is slight because operator error doesn't enter into the extent that it does in the citrate-dithionite extraction procedure.

In view of the small sample size and the fact that the samples were not ground, this coefficient of variation does not appear to be excessive. A search of the literature revealed nothing for comparison. Considering the heterogeneous nature of the spodosols, especially the spodic horizons, it is extemely difficult to achieve an average value for any particular horizon. In fact, each value obtained represents a true value for some portion of the horizon from which the sample came.

The same extracts on which iron was determined were further processed (see the aluminum analysis procedure) and analyzed for the aluminum content. The average coefficient of variation for the aluminum analysis was 14.50%.

An increase of 0.60% in the C.V. between the iron and aluminum determinations reflects primarily operator error.

The acidified ammonium oxalate extracting solution was the easiest to prepare of the three methods, and also the easiest to accurately add to the soil sample. The large amounts of solution required by the other procedures

(40 ml of sodium citrate or 76 ml of sodium pyrophosphate) necessitates the use of a graduated cylinder rather than a pipette to meter out and add solutions to the soil sample.

From 24 to 48 samples were extracted at one time. Forty-eight samples was considered to be the maximum number that could be extracted and still keep the total time of extraction within 30 minutes of the 4 hour extraction period. Several minutes are required to add the 10 ml of solution to each sample and time is also taken during the centrifugation period unless the centrifuge head is large enough to accomodate all of the samples at one time. Approximately 50 to 60 samples could be extracted per day, including weighing, extracting, organic matter destruction and dilution to a known volume.

The procedure used to destroy organic matter in the extracts also drives off the excess ammonium oxalate. The oxalate ion causes interference with the orth-phenanthroline iron determination. No interferences were found in the extracts when determining iron and aluminum on the Perkin-Elmer 303. Recovery experiments for both iron and aluminum revealed no interferences and complete recovery of added iron and aluminum was achieved.

#### Citrate-Dithionite Extraction Procedure

The citrate-dithionite extraction procedure of Mehra and Jackson (47) although designed primarily to clean up clays, has come to be the standard whereby extractable iron oxides are measured and other extraction procedures compared. Several researchers (18, 30, 33) have made comparisons against the citrate-dithionite method (47) when developing extraction methods of their own. McKeague and Day (43) and Franzmeier et al (30) wanted to develop extraction procedures which would be more specific for the characterization of Podzol B horizons. The citratedithionite procedure was felt to have shortcomings, especially in not permitting the determination of the amount of organic matter that was extracted. The extraction procedure is fairly complicated and subject to operator error, especially the maintenance of the 80°C. temperature and the number of stirrings. The other major shortcoming of the citrate-dithionite procedure is that too much of the fine crystalline iron particles are extracted and too little aluminum.

In this study, all of the soils were extracted by this procedure and the iron and aluminum contents of the extracts measured. Fifty-eight separate samples, primarily from the B horizons, were replicated from 2 to 4 times. The

results were analyzed by the computer and a coefficient of variation computed for each. The results showed the average coefficient of variation for the iron determination to be 9.40%. With the large (4 gram) sample size, the error due to sampling is not as great as it is with the oxalate extraction procedure. However, the operator error is probably much greater because the extraction procedure requires much more operator care. The temperature must be carefully maintained, the number of stirrings and the time of stirring is hard to keep uniform. Holmgren (33) devised a modified procedure whereby the operator error is cut down by carrying out the extraction at room temperature and letting a mechanical shaker do the shaking.

The same soil extracts on which iron was determined were further processed for the aluminum determination. The coefficient of variation for the aluminum determination is 10.37%. There is an increase of about 1% compared to the variation in the iron determination which is the result of operator error primarily, with a slight amount the result of analysis error.

Concerning the inability of the citrate-dithionite method to extract appreciable amounts of aluminum from soil samples, Drumbum et al (22) found that most of the aluminum in Wisconsin soils was complexed with silica as allophane.

That this extraction method does not remove much aluminum has been noted by several workers (2, 31, 43, 44, 47). Evidently the method does not extract much aluminum silicates.

The Comprehensive Soil Classification states that in the spodic horizon, aluminum is always present and probably essential (68, 69) but no methods to date have been used with the extraction of aluminum as the primary concern.

The presence of interfering ions in the determination of iron and aluminum in the Perkin-Elmer 303 was checked out. There were no interferences from either the sodium or citrate ions from this method on the iron determination. However, the sodium ion in conjunction with the aluminum ion created a positive interference in the aluminum determination. Excess citrate ion not destroyed by the organic matter destruction interfered with complete recovery of the aluminum in a precipitation procedure used to remove the sodium. Treatment of the aluminum standards in the same manner as the unknown samples negated the interferences.

Pyrophosphate-Dithionite Extraction Procedure

Franzmeier et al (30) set up predetermined parameters on the basis of field soil characteristics, and set out to

find ways of treating the soils in the laboratory to achieve the grouping they wanted.

A sodium pyrophosphate-dithionite extraction treatment was selected because of its ability to extract soil organic matter and organic-metal complexes from B horizons. This extractant was also chosen because there would be no interfering ions when determining the amount of organic carbon that was extracted from a soil sample. They also found that the pyrophosphate-dithionite extracted more aluminum from any given sample than the citrate-dithionite method regardless of the number of treatments.

The cation exchange capacity was found to be highly correlated with the pyrophosphate-dithionite extractable carbon (r=.98). An even higher correlation was obtained between CEC and total organic carbon (r=.99) of spodic horizons. There was also a good correlation between the combined amounts of extractable iron and aluminum and CEC.

From their studies Franzmeier et al concluded that the amorphous materials of spodic horizons consisted primarily of iron and aluminum organic complexes, and that the extra aluminum extracted had largely inorganic bonding which bears out the results of DeMumbum (22). One last point was raised, that of whether total rather than extractable carbon would work just as well as a criterion for separating spodic from other kinds of horizons.

Some 68 samples were extracted using the pyrophosphate-dithionite procedure in order to compare the author's technique and analysis methods (with those of the Beltsville laboratory method and results. Comparable results were obtained.

This author found that the pyrophosphate-dithionite extracting solution was the hardest to prepare and as the method requires the most solution volume per sample, the difficulty of extractant preparation was judged a hindrance to the procedure. The extraction time operator work per sample was also the longest of the three methods that were evaluated in this study.

No interferences were encountered when analyzing for iron with the Perkin-Elmer 303. Neither the sodium-pyrophosphate nor the orthophosphate ions interfered even at levels much higher than contained in the extracts.

The determination of aluminum on the Perkin-Elmer 303 presented difficulties. Both the sodium and phosphate ions caused a positive interference in the absorption readings. A precipitation procedure that would remove the sodium failed because of the solubility of aluminum and iron pyrophosphates even at a high pH. Because the detection of aluminum by atomic absorption means is still new, further research on phosphate and sodium interference is needed

before the aluminum values can be considered to be accurate. This interference problem wasn't encountered until the very last of the laboratory analyses. Proper treatment of the aluminum standards would cancel the interferences.

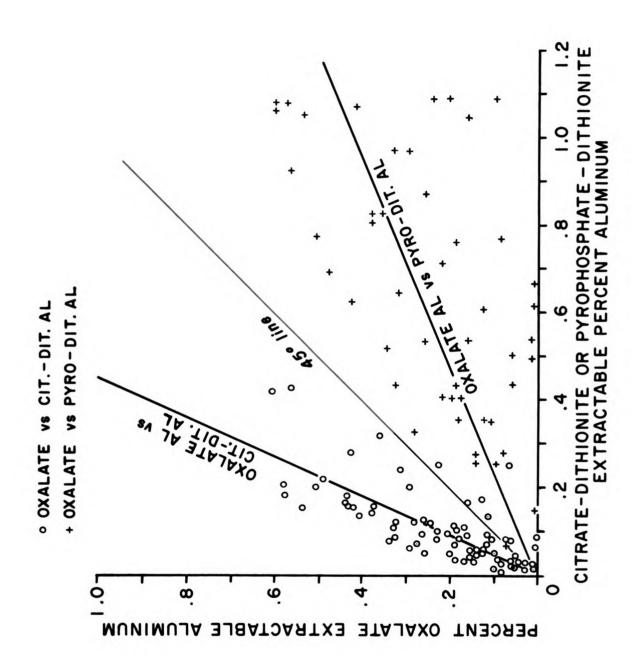
#### 5. Results and Conclusions on the Extraction Procedures

The primary purpose of this part of the study was to evaluate the spodic horizon criteria and classification for Michigan soils. At the same time, considering the number of soils and the wide range in characteristics, a comparison of methods used to determine pH, carbon, extractable iron and aluminum were also feasible.

All of the soils were extracted by the citratedithionite and oxalate procedures for extractable iron
and aluminum. The results appear in Table 13 in
Appendix III. Table 13 also shows the Beltsville Laboratory
values by the pyrophosphate-dithionite extraction procedure
on some of these same samples.

The ability of the oxalate procedure to remove more aluminum than the citrate-dithionite procedure is readily evident. Figure 3 shows this relationship. However, the pyrophosphate-dithionite method removed much more Al than the oxalate method.

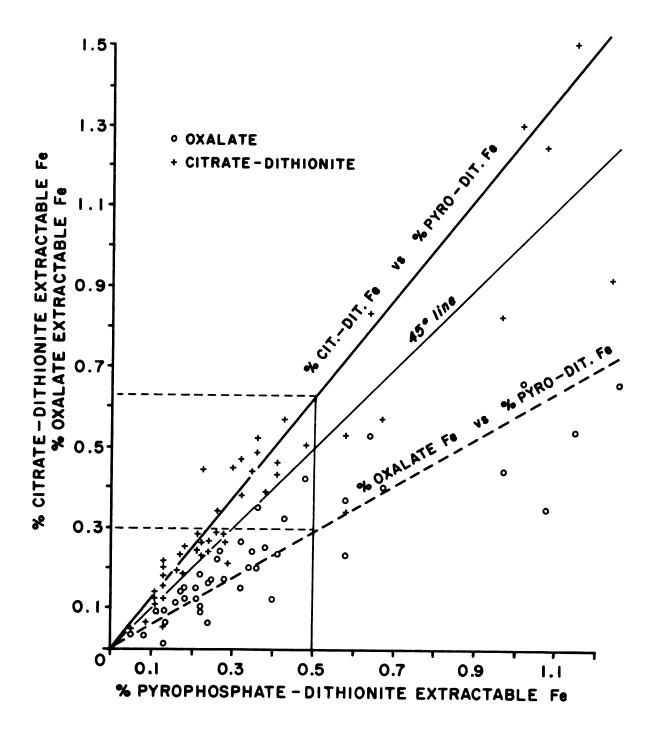
Figure 3. Comparison of Aluminum Extraction Methods.
Oxalate vs Citrate-dithionite or Pyrophosphate-dithionite



On the other hand, the citrate-dithionite procedure extracts slightly higher quantities of iron than the pyrophosphate-dithionite procedure and the oxalate method much lower quantities of Fe, Figure 4. Of course, the citratedithionite and pyrophosphate-dithionite methods extract amorphous as well as crystalline forms of iron, while the oxalate method extracts only the amorphous kind of iron compounds. This explains the differences in values. Only 3 oxalate iron values exceeded the citrate-dithionite values for any sample and none of the oxalate iron values exceeded pyrophosphate-dithionite iron values for any sample. Of 170 samples, 82 had higher amounts of oxalate extractable aluminum than oxalate extractable iron. In some cases, even higher than the citrate-dithionite extractable iron values for particular horizons. Out of 170 samples, 24 yielded higher amounts of citrate-dithionite extractable aluminum than oxalate extractable aluminum for particular samples. Seventeen of the samples that did this were from 02, Al, A2 horizons, or from horizons below the spodic horizon.

McKeague (44) compared the oxalate method with the pyrophosphate-dithionite method. Of the two procedures, McKeague concluded that the oxalate extraction procedure was much simpler and was able to distinguish Podzols and subgroups within the Pdozols from other classes of soils.

Figure 4. Comparison of Iron Extraction Methods: Oxalate or Citrate-Dithionite, vs Pyrophosphate-Dithionite

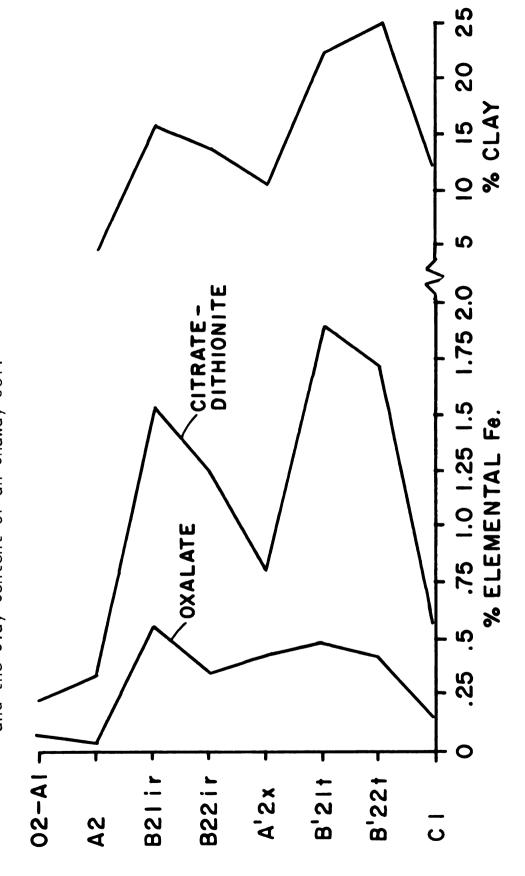


McKeague concluded that the pyrophosphate-dithionite extraction procedure was less specific because it removed crystalline iron compounds from the soil, especially from soils high in clay. Figure 4 illustrates the differences in the three extraction procedures for iron.

The Onaway, McBride, and Munising soils in this study all showed increases in iron content with increasing clay content of the sample, when extracted with pyrophosphate-dithionite or citrate-dithionite. In this respect the pyrophosphate-dithionite and citrate-dithionite extraction procedures are similar. Both fail to differentiate between amorphous and crystalline forms of iron in soils. The oxalate iron values for these same soils showed only slight increases of iron with increasing clay content. This indicates that the oxalate method differentiates between amorphous and crystalline iron as suggested by others. Figure 5 illustrates this for an Onaway profile.

McKeague (44) also concluded that the extractable carbon that could be determined in the pyrophosphate-dithionite extracts did not appear to have any major advantage over using total carbon. He concluded that the extractable carbon in any particular horizon did not clearly differentiate podzol B horizons from other subsurface horizons, that total carbon was as useful and that by using

Relationship of Extraction Method to Percentage of Iron Extracted and the Clay Content of an Onaway Soil Figure 5.



total carbon one analysis step was saved. Franzmeier also found that the total carbon content of a spodic horizon correlated as well with the cation exchange capacity of the spodic horizon as extractable carbon did (29). This writer agrees with McKeague that the simplicity of the oxalate extraction method, compared to the other two extraction methods, and the oxalate extractable iron and aluminum values separated soils better in the classification system than the citrate-dithionite or pyrophosphate-dithionite extractable iron and aluminum values. Only slight adjustments would be necessary in the spodic horizon criteria to use total rather than extractable carbon, as discussed later.

#### III. RESULTS AND DISCUSSION

# A. <u>Development of a Rapid Field or Laboratory Test for the Determination of Spodic Horizons</u>

With the adoption of the Comprehensive System of Soil Classification greater stress has been placed on the quantitative aspects of soil morphology and genesis. The use of moist horizon colors of "podzol B's" in the field as a criterion for spodic horizon classification is very uncertain. Reddish colored parent materials may mask the effects of podzolization.

It was therefore deemed desirable to evaluate chemicals that may be able to extract materials from spodic horizons in the field, with the possibility of correlating the color of the extract with the amounts of extractable carbon, iron, and aluminum in the horizon as determined in the laboratory. Such a quick test would help the field man make positive identifications of spodic horizons.

Several chemicals were considered and evaluated for their ability to extract highly colored substances from soil horizons. They are:

> Saturated sodium pyrophosphate, Saturated ammonium oxalate, Saturated ammonium oxalate and saturated oxalic acid in a 1:1 ratio,

Saturated sodium pyrophosphate and saturated sodium dithionite in a 4:1 ration, Saturated sodium dithionite, Saturated sodium citrate, and EDTA solution

All of these solutions were tried on soil materials known to qualify as spodic horizons as well as on some complete mineral soil profiles.

The Hellige-Truog spot plate was chosen as the most suitable container because of its wide spread use in the field. One soil, Hiawatha sand, that has a known spodic horizon was used to make all necessary comparisons. A saturated solution of sodium pyrophosphate was used to evaluate the time of extraction.

Ratio of Soil to Solution and Time of Extraction
 The first test consisted of filling the spot plate

full of soil, adding three drops of extractant, stirring until mixed, and adding a filter strip after a three minute interval. This procedure, although it produced the strongest colors, was judged unworkable because of the low liquid contents.

The next series of trials consisted of filling the spot plate 1/2 full of soil and adding 5 drops of liquid. This filled the spot plate depression. The suspension was stirred until well mixed. Extraction periods of three, five, ten, fifteen, and twenty minutes were evaluated.

In all cases, the longer the period of extraction the darker the extract became and the darker the filter paper color. Table I shows the results of the color tests in Munsell color notations. The results show that for extraction times of less than 10 minutes the filter paper colors were lighter. The extract color for extractions over 10 minutes showed little color difference from the 10 minute extraction. On this basis an extraction time of 10 minutes was chosen.

Table 1. Effect of time of extraction and color of extracts of horizons of Hiawatha sand

Sample	3 min.	5 min.	10 min.	15 min.	20 min.
31-3-1 Al 31-3-2 A <sub>2</sub> 31-3-3 Bh 31-3-4 Bhir 31-3-5 B <sub>3</sub> 31-3-6 Cl 31-3-7 C <sub>2</sub> ortstein	10 YR7/3 7.5YR7/3 10YR6/3 10YR7/4	10YR6/4 10YR7/2 10YR5/4 10YR7/3 10YR7/2 NC NC NC 7.5YR4/4	7.5YR5/4 10YR7/2 7.5YR4/4 10YR5/6 10YR5/3 NC NC NC 7.5YR5/6	7.5YR5/6 10YR7/2 7.5YR5/4 7.5YR5/6 10YR7/3 NC NC NC 5YR4/4	10YR7/2 5YR4/4 7.5YR5/6 10YR7/3 NC NC

NC = no color

The slight variability of hues and value after 10 minues was found to be insignificant.

# 2. Effect of Stirring

The effect of the number of times of stirring during extraction was considered next. The plate was filled 1/2 full of soil, 5 drops of liquid was added and the mixture was stirred once, immediately. The next test was the same except the mixture was stirred immediately after the solution was added and again just before inserting the filter paper. The last test consisted of stirring at the beginning, half way through, and just before adding the filter paper. During this series of tests the time of extraction was kept constant at 10 minutes. The results in Table 2 showed that stirring three times during extraction generally resulted in darker colors.

Table 2. Effect of stirring on color extracts of horizons of Hiawatha sand

Sample	Nur	mber of Stirrin	gs
	once	twice	three
31-3-1, A1	7.5YR5/4	10YR6/4	7.5YR5/4
31-3-2, A2	10YR7/2	10YR6/3	10YR6/3
31-3-3, Bh	7.5YR4/4	10YR5/6	7.5YR4/4
31-3-4, Bhir	10YR5/6	10YR6/4	10YR5/6

## 3. Effect of Temperature

Using the same soil as in all previous tests, a constant time of extraction (10 min.) and three complete stirrings, the effect of temperature on extraction was next evaluated. Temperatures of soil and extractant of 40, 48, 58, 66, and a lab. temp. of 75-80°F. were used. Table 3 shows the effect of temperature on the pyrophosphate extractions of soil horizons. A minimum field soil temperature of 66-70°F. would be necessary in order to have the darkest colored extracts. From the results the effect of temperature is very pronounced below 66°F. Above this temperature there was no significant difference in extract colors. The poor colors resulting from low temperatures limit the use of the test in the field.

#### 4. Effect of Extractants

Table 4 lists five of the extractants that were evaluated and the extract colors that resulted. EDTA and sodium citrate extractants, although able to extract sesquioxides from podzols, produced extracts that had no color that could be picked up on filter paper and those tests are not recorded in the table.

Effect of temperature on color of pyrophosphate extracts of horizons of Hiawatha sand\* Table 3.

Sample	Hor.	400F.	48 <sup>0</sup> F.	58 <sup>0</sup> F.	66°F.	Lab. (75-80 <sup>0</sup> F.)
31-3-1	A1 A2 B21hir B22ir	10YR8/3 10YR7/2 10YR6/4 10YR7/4	10YR7/3 10YR7/2 10YR6/4 10YR7/4	10YR7/3 10YR7/2 10YR5/4 10YR7/4	10YR6/4 10YR7/2 7.5YR5/4 10YR6/4	10YR5/4 10YR7/2 7.5YR4/4 10YR6/4
**************************************	**************************************	12/40 04:7				

\*Note: One stirring only!

Comparison of extractants and extract colors on horizons of Hiawatha sand Table 4.

Sample	Hor.	Saturated Na- Pyrophosphate	Sat. Na- Pyrophosphate + +Sat. Dithionite	Saturated NH4 Oxalate	Saturated Na- Dithionite	Oxalic Acid + Sat, NH <sub>4</sub> Oxalate
31-3-2	A1	7.5YR5/4	10YR6/4	10YR8/3	5Y8/4	N.C.
	A2	10YR7/2	10YR7/2	10YR8/1	5Y8/4	N.C.
	B21hir	7.5YR4/4	7.5YR5/6	7.5Y5/4	2.5Y7/8	2.5Y8/4
	B22ir	10YR5/6	10YR7/2	10YR7/4	2.5Y8/8	5Y8/3

The saturated sodium dithionite produced yellow colors. The yellow may be due to the iron in the sample. It was difficult to distinguish between the shades of yellow using the standard Munsell color chips that are used by soil scientists. The other objection to sodium dithionite was its objectionable odor. Although this extractant had promise it was rejected on the basis of the objectionable odor.

The pyrophosphate extractant containing sodium dithionite was also rejected because the plain pyrophosphate produced as dark or darker colors.

The saturated ammonium oxalate was second choice among the chemicals tested. The ammonium oxalate was rejected because of its slightly poorer performance and its poisonous nature. The ammonium oxalate extractant appeared to be more specific than the pyrophosphate in extracting certain kinds of organic matter.

Table 5 compares the extract colors from 02 and B horizons of two podzol profiles. Both the pyrophosphate and the oxalate extractants produced comparable colors from the Munising podzol B horizons, but the pyrophosphate gave darker colors in both the 02 horizons.

Extractants and colors of extracts of  $0_2$  and B horizons of  $0_1$  and  $0_2$  and  $0_3$  and  $0_4$  and  $0_4$  and  $0_4$  and  $0_5$  are  $0_5$  and  $0_5$  and Table 5.

Soil Series	Sample Hor.	Hor.	Saturated Pyrophosphate	Saturated NH4 Oxalate % T.C.**	% T.C.**	Estimated % Ext. C.*
Onaway	21-3-1	02	5YR3/4	7.5YR5/4	7.99%	79.
	21-3-3 B21ir	B21ir	10YR5/4	10YR7/4	1.03	.75
Munising	31-2-1	02	7.5YR5/4	10YR8/4	5.12	1.38
	31-2-3	B21hir	5YR3/4	5YR3/4-3/3	3.17	2.31

\*Calculated 73% of T.C. in subsurface horizons and 25% of T.C. in surface horizons.

\*\*T.C. - Total Carbon

# 5. Trials on Organic Soil Horizons

Although sodium pyrophosphate is used to distinguish sapric from fibric horizons in organic soils, a test comparing pyrophosphate (pH 10), with ammonium oxalate (pH 6.5), and acidified ammonium oxalate (pH 1.5), on the color of extracts from some horizons of organic soils gave the results shown in Table 6. Also shown in the table are the suspension pH's after extraction, where those were noted. The acidified ammonium oxalate produced only slightly colored extracts from the samples tested and no significant color differences were noted as seen in the last column of the table below. The ammonium oxalate and pyrophosphate both gave dark extracts from the sapric organic material and very little color from the other materials.

Table 6. Extraction of organic materials by different reagents with the resulting colors of extracts and final pH's.

Sample		Extractant and In	itial pH
	pyro., pH 10	am. ox. pH, 6.5	acid am. ox. pH. 1.5
Sapric	5YR3/4, pH 5	5YR4/4, pH 8	5Y8/3, pH 2
Hemic	10YR7/3	2.5Y8/4	5Y8/2
Sed. Peat	10YR8/2	10YR8/1	N.C.
Marly Peat	2.5Y8/2, pH 10	10YR8/1, pH 8	2.5Y8/2, pH 6

It is interesting to note the pH's after extraction. The pyrophosphate pH, decreased except on the marly sample. The ammonium oxalate pH's increased as did the acid ammonium oxalate. This suggests that the reagents may extract different components at different pH's.

## <u>Procedure</u>

Using the standard Hellige-Truog spot plate, fill the cavity one-half full of soil. Add 5 drops of extracting solution, to fill the cavity, and stir until mixed. Let stand for 5 minutes and stir again. Let stand for another 5 minutes, then stir and insert a strip of filter paper. Remove the filter paper after the wetting front has climbed about 1/2-inch up the paper. Let the paper dry until the water sheen is gone. Read the color of the part of the strip between the suspension contact zone and 1/4-inch above it. This procedure was designed to be done during the time that a profile description was being made in the field. The air and sample temperatures must be about 70°F. for accurate results. The laboratory procedure is the same.

#### 6. Trials on Several Mineral Soils

The quick test procedure was tried on several mineral soil exhibiting varying degrees of podzolization in order to determine whether there was any correlation between the extract color and the amounts of total carbon, extractable

iron and aluminum contained in the B horizons of the soils.

Figure 6 shows the relationship of the Munsell color value of the extracts to the percent total carbon contained in all Prozol B horizons of all soils tested. There is an apparent difference between the extract colors from sands and sandy loams or loams. Larger carbon contents were associated with Munsell color values of 5 or less on the finer soil samples. Van der Voet (76) found the same relationship of soil texture to the carbon content of Podzol B horizons in New Hampshire soils.

Figure 7 shows the relationship between the Munsell value notation of the extracts and the total extractable amorphous materials. A value of 73% of the total carbon value of the B horizons was used to determine an approximate value for extractable carbon. Actually there may be no advantage of using extractable carbon values from subsurface horizons. Both values are reported to correlate with the CEC. and the extractable carbon, where it has been determined, is a nearly constant proportion of the total carbon. If total carbon plus extractable iron and aluminum were plotted in Figure 6, the curves would have the same shape, but be shifted to the right.

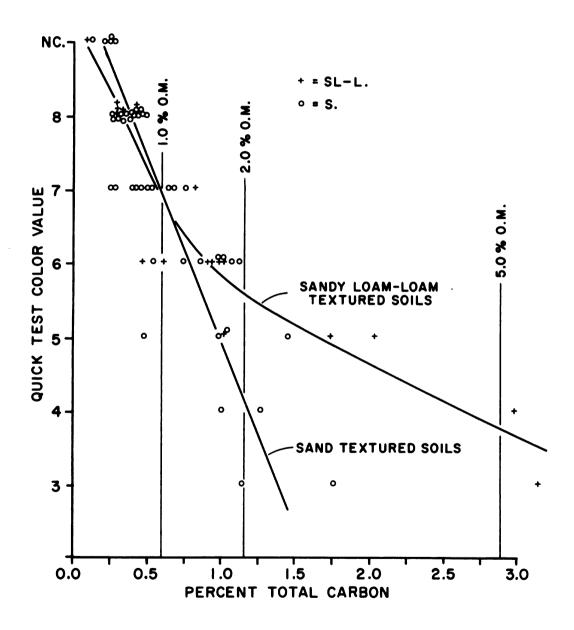
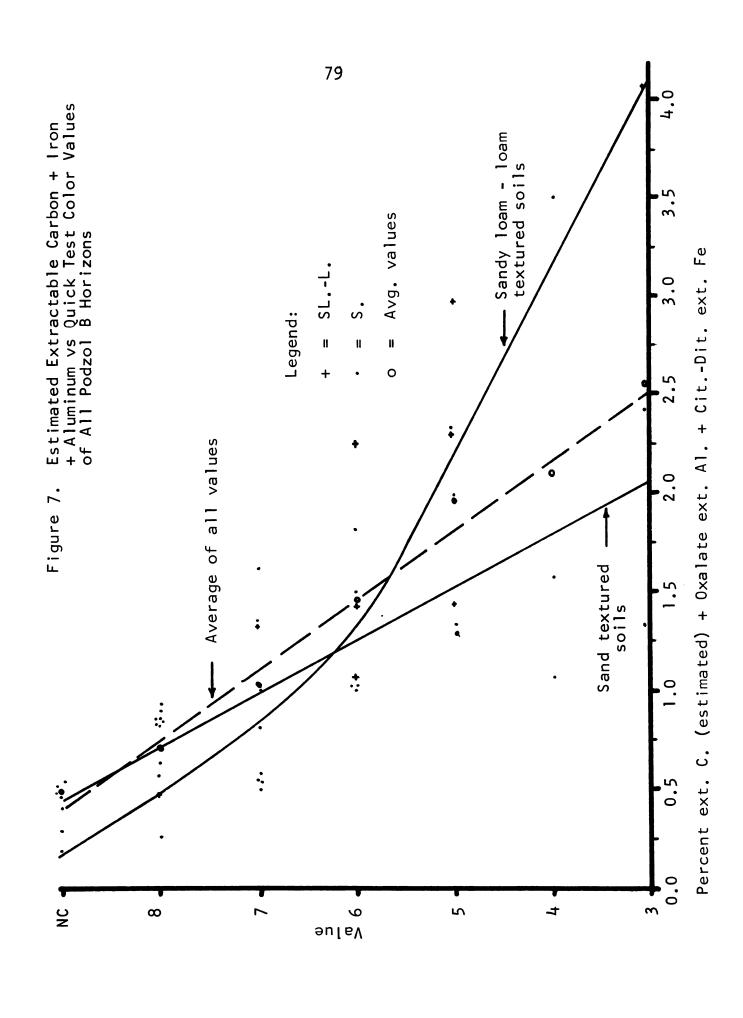


Figure 6. Percent Total Carbon vs Quick Test Color Value of all Podzol B Horizons



In Figure 8 the total extractable amorphous materials are shown arranged in a plot of values vs chromas of the extracts. There appeared to be a natural break between color values of 7 and 8 and chromas of 2 and 3 as shown by the line.

Table 7 lists the soil samples with the strongest spodic character in each profile and the classification of each profile. From the data in Table 7, values of 6 or less and chromas of 3 or more from the quick test color would qualify a B horizon as having sufficient amorphous materials to qualify as a spodic horizon in the Comprehensive Classification System. The Vilas, Rousseau and possibly the second Rubicon B's all qualify as spodic horizons but did not pass this quick test.

#### 8. Possible Improvement in Method

With the realization that the Quick Test had possibilities for separating soils on the basis of the extract color, further tests were made on the effect of temperature on the extract color and to determine if the quantity of soil was critical in its effect on the extract color.

Table 8 shows the results of the experiment.

Data columns 1 and 2 of Table 8 list the results obtained at two different temperatures using the standard

Figure 8. Percentages of Oxalate Al + Citrate-dithionite Fe + Estimated Extractable Carbon plotted on a Graph of Color Values vs Chromas of the Quick Test

NC _	.323 .565 .568 .524 .677	.413					
8	.582 .489 .800 .802						
7	.565 .808 .474		.761 .628	.841 1.030 1.345			
Value 9				2.237 1.419 1.870 1.581 1.147 1.156			
5					2.379 2.317 1.402 2.072 1.587 1.388		2.950
4					3.579 1.122 1.669		
3					4.191 2.424 1.342		
	1		2	3	4	5	6

Chroma

Quick test and horizon colors as related to soil classification Table 7.

Soil	Horizon	Spodic Hor.	Quick Test Color	Horizon Color	Classification
Rubicon (vilas)	B21ir	yes	10YR6/3	5YR3/4	Entic Haplohumod or Entic Haplorthod
Munising	B21hir	yes	10YR4/4	5YR3/3	Alfic Fragiorthod
Vilas	B2lir	yes	10YR7/1	5YR3/4	Entic Haplohumod or Entic Haplorthod
0mega	821	OU	10YR8/1	5YR4/4	Typci Udipsamment
Rousseau	B21ir	yes	10YR7/2	5YR4/4	Entic Haplohumod or Entic Haplorthod
Grayling	B21	OU	10YR8/1	7.5YR4/4	Typci Udipsamment
Rubicon	B21ir	yes	10YR8/1	5YR4/4	Entic Haplohumod or Spodic Udipsamment or Entic Haplorthod
Grayling	821	OU	10YR8/1	7.5YR4/4	Typic Udipsamment
Onaway	B21ir	yes	10YR5/6	5YR3/4	Alfic Haplorthod
Onaway	B21ir	yes	10YR6/3	5YR3/4	Alfic Haplohumod or Alfic Haplorthod

Table 7. continued.

Soil	Horizon	Spodic Hor.	Quick Test Color	Horizon Color	Classification
Kalkaska	B21h	yes	7.5YR4/4	5YR2/2	Typic Haplohumod or Entic Haptohumod or Entic Haplorthod
Hiawatha	B21hir	yes	5YR3/4	5YR2/2	Typic Haplorthod
Munising	B21hir	yes	5YR3/4	5YR3/4	Alfic Fragiorthod
Hiawatha	B21h	yes	5YR3/4	5YR2/2	Typic Haplohumod or Typic Haplorthod or Entic Haplorthod
McBride	B2ir	yes	10YR6/3	5YR 3/4	Alfic Fragihumod
Oakville	B21*	no	10YR7/1	7.5YR4/4	Typic Udipsamment
Omega	B21*	no	10YR7/2	7.5YR4/4	Typic Udipsamment
McBride	B2ir	yes	10YR5/4	5YR3/2	Alfic Fragihumod
Kalkaska	B21h	yes	5YR3/4	5YR2/2	Entic Haplorthod
Eastport	81	OL	10YR7/1	7.5YR5/4	Spodic Udipsamment

Pyrophosphate quick test color values of 7 or less and chromas of 3 or more all qualify as spodic horizons. B horizons that do not pass this test are those in the Entic subgroups of Haplohumods or Haplorthods or are Udipsamments. Note:

\*Horizon is not deep enough to qualify as spodic.

Influence of temperature and amount of soil comparisons on Quick Test colors Table 8.

	•	•			
Soil	Horizon	Standar	d Method	Incre Soil A	ased mount
·		75-80°F. (Col. 1)	70°F. (Col. 2)	75-80°F.	70°F. (Col. 4)
Rubicon	B21ir	6/3-7/3	-	6/3	-
Munising	B21hir	4/4-5/4	-	-	-
Vilas	B21ir	7/1-8/1	8/1-NC	7/3	-
0mega	B21	8/1-NC	-	8/1	-
Rousseau	B21ir	7/2-8/1	7/1	6/3	7/2
Grayling	B21	8/1-NC	NC	8/1	8/1
Rubicon	B21ir	7/1-8/1	-	8/2	-
Grayling	B21	8/1-NC	-	8/1	-
Onawa y	B21ir	5/4-5/6	6/3	-	-
0nawa y	B21ir	5/3-6/3	-	-	-
Ka 1 kas ka	B21h	4/4-5/4	-	-	-
Hiawatha	B21hir	3/4-5/4	-	-	-
Munising	B21hir	3/4-4/4	-	-	-
Hiawatha	B21h	3/4-4/4	-	-	-
McBride	B2ir	5/3-6/3	-	-	-
0akville	B21	7/1-8/1	8/1-NC	7/3	-
0mega	B21	7/2-8/1	8/1	7/3	8/2
McBride	B2ir	5/3-6/3	6/3	-	-
Ka 1 kas ka	B21h	3/4-4/4	-	-	-
Eastport	В1	7/1-8/1	8/1	6/3	7/2

Note:

The Hue is unimportant.

Column I gives the color range found in the laboratory.

The samples in Columns 2, 3, 4, are those of soils which are on or close to the borderline of qualifying.

procedure listed earlier. In data columns 3 and 4 the amount of soils was increased from filling the spot plate cavity one-half full to 3/4 full. Columns 1 and 3 show the results of the higher temperature likely to be encountered in the laboratory with varying soil amounts, while columns 2 and 4 list the results of the lower temperature (70°) likely to be found under field conditions with varying soil amounts. The soils tested in columns 2, 3, 4, and on those soils in this study which on the basis of the quick test results, fall in an area where the test is inconclusive. Some of these soils had spodic horizons according to the chemical data but had quick test values of 7, which do not clearly place a soil in the spodosols or definitely put it into some other groups but with increased soil content, the value of 7 and chromas of 3 would place a soil in the spodosols. A comparison of the results in columns 1 and 2 showed a decrease of color with the change in temperature from 75 to 80 down to 70°F, but keeping the soil amount constant. Columns 3 and 4 also showed the same relative decrease in color with lower temperature. It seems a temperature of 75-80° will give darkest colors. Columns l and 4 show that even with lower temperatures, but with increased soil amount the results are nearly the same.

The increased soil amount was therefore incorporated into the Quick Test instructions that went to the field soil scientists and that appear in the summary to this section.

Table 9 is a compilation of the results of the Quick Test using the spot plate filled 1/2 full of soil under field conditions. The test was conducted at intervals during September, 1967 in Clare County, Michigan. author expresses his appreciation to Johnny Collins who made the field tests and the laboratory tests later). All of the soils that were tested have been classified as Spodosols on the basis of field characteristics. The soil temperature in column 6 is at a 20 inch depth. The Quick Test results substantiate the placement of the soils in the classification system. Listed are the Quick Test results under field conditions and laboratory conditions 6 months later when the soils were air dry. There is a decrease of chroma in most cases after the soils were air dry. The variations that are evident are believed to be the result of slightly different operator techniques; the variation in lighting; the ability to read the extract colors; or possibly small differences associated with air drying. It should be stated here that the color value of the extract is the most important, the chroma is considered

Laboratory comparisons with field results from Clare County, Michigan September, 1967Table 9.

Soil	Quic air dry	Quick Test air dry field moist	Horizon color	Soil temp. at 20" depth	Classification
Kalkaska 1	9/5	8/5	5YR3/4	62°F.	Entic Haplorthod*
Kalkaska 2	4/2	5/4	5YR3/2	62	Entic Haplorthod*
Menominee	6/3	8/9	5YR4/3	65	Alfic Haplorthod
Mancelona	4/9	8/9	7.5YR5/6	49	Alfic Haplorthod
Rubicon 1	4/9	8/5	5YR3/3	62	Entic Haplohumod*
losco	9/9	5/4	5YR3/4	62	Aqualfic Haplothod
Rubicon 2	4/9	9/5	7.5YR4/4	19	Entic Haplohumod*
Augres	4/4	9/5	7.5YR4/4	58	Entic Haplaquod

\*The present classification of Kaskaska is listed as a Typic Haplorthods.

Note:

The air dry Quick Test was conducted in the laboratory at a temperature of 78-80°F. The field test was conducted at the soil temperatures shown. The air temperature was in the 70°s. On the basis of the Quick Test plus other spodic horizon requirements, all of these soils would have spodic horizons with the possible exception of the two Rubicon soils. Some Rubicon will have spodic horizons while other Rubicon from other areas may not.

after the value. Only slight differences are evident when considering the value notations between field and air dry conditions, some decreases and some increases were noted on air drying but in no case was the difference more than one unit.

The Quick Test when used along with the horizon color, depth, and thickness will provide the field soil scientist with a means of more accurately determining whether a particular soil has a spodic horizon or not. As field data from Quick Test results are compiled, along with more laboratory data on other soils, there will be more chance to evaluate the current classification and correlation of soils in the Podzol soil region.

Following is the modified Quick Test procedure and the interpretations of the extract colors. It summarizes the temperature conditions, the modified procedure and the interpretations based on the soils tested to date on which there are laboratory data.

### 7. Modified Quick Test and Its Interpretations

This Quick Test was designed to be done in the field, or in the office under certain temperature conditions. The saturated pyrophosphate solution concentration is dependent on the temperature, with the contentration falling off rapidly below 70°F. Our experience to date indicates that

the tempeature of the pyrophosphate solution should not be below 70°F. (During the months of June, July, August, and September the air temperature and surficial soil temperature (about 20") will be high enough to give an average temperature of the soil-solution in the spot plate of 70 to 75°F. in Michigan.) The test can be done during the time it takes to write a soil profile description. During parts of the mapping season it will be necessary to collect small samples, bring them into the office and run the test there. The procedure is as follows:

## Procedure:

Using the standard Hellige-Truog spot plate, fill the cavity 3/4 full of soil. Add 5 drops of a saturated pyrophosphate solution, or enough to fill the cavity, and stir until well mixed. Let stand for 5 minutes and stir again. Let stand for another 5 minutes, then stir and insert a strip of filter paper. (Strips of filter paper 1/4" x 1" are used). Remove the filter paper after the wetted front has climbed 1/4-1/2" up the paper, further wetting dilutes the color. Let the paper dry until the water sheen is gone. Read the color of the part of the strip between the suspension contact zone and 1/4" above it. The time required for this test is about 15 minutes.

# <u>Interpretation of Results:</u>

Experience to date with Michigan samples analyzed in the Beltsville and East Lansing laboratories indicate that test color values of 7 or lower and chromas of 3 or higher, qualify any particular B horizon as having sufficient iron, carbon, and aluminum to meet the spodic horizon requirements. Values of 8 or higher and chromas of 2 or less eliminate the horizons as spodic horizons. Values and chromas of 7/1 and 7/2 from upper subsoils are from either the Entic Haplorthods, Entic Haplohumods, or Udipsamments. Other spodic horizon requirements must also be met, e.g. thickness, depth, continuity and horizon sequence. Soils sampled to date include the Omega, Grayling, Oakville, Eastport, Vilas, Rubicon, Hiawatha, Kalkaska, McBride, Munising and Onaway series. No spodic Ap horizons have been tested.

Other tentative guides available for higher amounts of soluble components based on very few examples, are as indicated in Figure 6. Sands with test values of 4 or less and loams with test values of less than 6 have organic carbon contents of 1.16% or more (2% organic matter). Loams with test values of 4 or less have organic carbon contents of 2.9% or more (5% organic matter).

## B. Use of Chemical Data to Classify Soils

The soils involved in this study were formerly classified as Podzols, and Brown Podzolic (or Regosols or dry sand) soils. With the advent of the 7th Approxmation and the adoption of the Comprehensive soil Classification System, the use of chemical, physical and mineralogical characteristics gained new stature. The present classification of Spodosols depends largely on the chemical characteristics of the spodic horizon.

The podzolization process involves the addition of organic matter to the soil surface and subsoil, leaching of bases to lower positions in the profile, and the formation of mobile sesquioxides with organic matter, their transportation to and redeposition at lower positions in the profile. In view of this, it was believed desirable to measure the amounts of iron, aluminum and carbon that were the result of soil forming processes in the Podzol B horizon, as a means of separating the various classes of Podzols that were formerly called Brown Podzolic and minimal, medial or maximal Podzols.

Because field properties or geographic associations such as soil color, pH, natural vegetation, physiographic position, and relative age often led to difficulties in properly classifying, both field and laboratory criteria were proposed in the new system. Appendix I, an abbreviated version of the 1967 supplement to the 7th Approximation, is the Comprehensive Soil Classification section dealing with the soils in this study as modified to June 1968.

In this approach some problems to be solved were what analytical procedures should be used to extract carbon, iron, and aluminum from Podzol B horizons, and what did the values that resulted mean? It has been well established that the extraction procedures using sodium dithionite, extract forms of iron other than the amorphous kinds which are thought to be due primarily to recent soil forming processes. In the United States the soil survey criteria for the spodic horizon is currently based on the amounts of pyrophosphate-dithionite extractable carbon, iron and aluminum in spodic horizons (9). In Canada (52) an acid ammonium oxalate extraction procedure has been chosen to remove amorphous iron and aluminum from soils. Because Canada has a far greater acreage of Podzols than the United States, it was deemed desirable to compare the

two extraction procedures and classification systems.

Another purpose of this study was to test the current spodic horizon classification criteria in use in the United States on Michigan soils.

Table 12 in Appendix III lists the laboratory data for the soils that were studied, arranged in numerical order of the profile sites as shown by the first two numbers in the first column. This table lists the data of the author for the oxalate and citrate-dithionite extractions for all of the horizons of all of the soils that were sampled plus total carbon values from an induction furnace (Leco) carbon analyzer. It also lists the data from the Soil Conservation Service, Beltsville Laboratory from the pyrophosphate-dithionite extraction as well as the clay content of each horizon, and the Walkley-Black carbon contents.

As was stated earlier in this paper, the oxalate aluminum values are much higher than the citrate-dithionite aluminum values. On the other hand, the citrate-dithionite iron values are in most cases higher than the oxalate iron values. The oxalate extraction method evidently is a more efficient extractor of aluminum than the citrate-dithionite method. The citrate-dithionite iron values correspond closely to the pyrophosphate-dithionite iron values, but average somewhat greater. Both the citrate-

dithionite and pyrophosphate-dithionite iron values correlate closely with the clay content of the sample, because these two extraction methods also attack crystalline forms of iron in the clay fraction of the sample. A comparison of the iron values with the clay contents for the Onaway soil shows this relationship. The oxalate iron values also increase with increasing clay contents but to a much lesser degree. Figure 5 illustrates this.

The pyrophosphate-dithionite aluminum values are in nearly all cases higher than the oxalate aluminum values by a factor of from 2 to 4 times, Figure 3. McKeague (44) in comparing the two methods, found that the oxalate aluminum values often exceeded the pyrophosphate-dithionite aluminum values, or if the pyrophosphate-dithionite aluminum values were greater, the difference was not significant. Some of the pyrophosphate-dithionite aluminum values reported here must be questioned: For example; Grayling 21-1 has 1.47% aluminum by the pyrophosphate-dithionite extraction and only 2.1% clay while the Onaway 21-3 has .78% oxalate aluminum and 8.2% clay. If that much aluminum is actually in the Grayling soil then how did it get there? The data reveal the need for more research on the amount of readily extractable aluminum compared to total aluminum or readily replaceable aluminum.

The use of the Podzol B horizon color to determine whether a soil has the properties of a spodic horizon has been found to give difficulties at times, especially with colors in the 7.5YR hue. Hues of 5YR2/2 which are dark enough for a horizon to be considered spodic, still does not tell the whole story of the composition of the amorphous extractable materials. The color notations of the B2lh horizons of both the Kalkaska soil (24-1-3) and Hiawatha soil (31-3-3) are 5YR2/2, Appendix II. Yet upon close examination of the data in Table 12, Appendix III, large differences in the amounts of carbon, aluminum and iron are evident. The Hiawatha spodic horizon contains much larger amounts than the Kalkaska spodic horizon. There is sufficient difference in the spodic horizons of these two profiles that Kalkaska would now be classified as an Entic Haplohumod while the Hiawatha would be classified as Typic Haplohumod. A combination of factors are evidently responsible for the development of color of the spodic horizon. Among these factors are: 1. Total amount of organic carbon and its degree of dispersion, 2. Texture of the horizon, 3. The degree to which the carbon masks the iron color, 4. The amount and degree of hydration of the iron. Evidently aluminum compounds do not contribute any

appreciable color to the spodic horizon. The lightest colored ortstein chunks may have more or less aluminum than the darker colored chunks which usually contain more carbon and iron or carbon, as shown in Table 13 in Appendix III.

Two soils, Rubicon (2-1) and Kalkaska (67-2) contained sufficient amounts of ortstein so that the samples could be subdivided into light and dark chunks by visual appearance. Equal amounts of the chunks were removed, and the remainder crushed and mixed to give an "average" value for the Ortstein. Table 13, Appendix III, shows the individual oxalate extracted iron, and aluminum with the total carbon values. With the separation of the light and dark chunks it was hoped that more could be learned about the composition of the ortstein and its cementing agents.

The data show that the lighter chunks generally had lower extractable iron and aluminum contents and lower total carbon contents than the darker chunks in the Rubicon 2-1. The Kaskaska ortstein 67-2-11 was similar but the light ortstein had higher aluminum contents. The generally high carbon, iron and aluminum contents of the ortstein chunks, than the minimum for the enclosing horizons, suggests that these complexes may all play a role in the cementation of the ortstein. However the composition of

the chunks were generally within the range of composition of the B horizons in which the ortstein was found.

If the intensity of the podzolization process can be measured by the amounts of extractable iron and aluminum in the spodic horizon, then the Kalkaska soil, which may be no older geologically than the Rubicon, is in a more advanced state of development. Why the process intensity is greater in the Kalkaska than the Rubicon can be ascribed in part to the difference in parent material. Matelski and Turk (42a) found that the Kalkaska parent material contained a larger quantity of easily weatherable Fe-Mg minerals than the Rubicon parent material. The iron and aluminum compounds probably would begin to be eluviated at the same time because of initially similar climates and vegetation succession in both soils, but would be eluviated in larger quantities in the Kalkaska soil enabling the development of an illuviated B horizon with greater rapidity. As the illuviated horizon developed to an extent where it influenced the downward percolation of water, possessed CEC., and contained organic matter which was being slowly broken down to furnish nutrients, Ca and Mg as well as nitrogen; hardwood vegetation more demanding for nutrients and water would gradually take over from the conifers in the Kalkaska soils. Also if there was a fire

and the surface organic matter were burned away, the organic matter contained in the spodic horizon would be available to furnish nutrients to the emerging plant roots. The Rubicon on the other hand when fire occurred, would have a smaller supply of organic matter available to furnish nutrients to new plant growth. Once hardwood vegetation invades a conifer stand, the podzolization process intensity increases again because of the higher polyphenol contents of the leaf leachates. This is probably why the Kalkaska soil is much more highly developed than the Rubicon. The combination of better parent material and faster vegetation succession enabled the Kalkaska soil to attain a degree of development surpassing the Rubicon soil. Given enough time, the Rubicon soil might develop to the stage that Kalkaska soil is today. Both Franzmeier (29) and Messenger (48) have shown that when hardwood vegetation succeeds conifers, with the exception of hemlock, that the podzol B development has increased.

A distinct but small clay bulge occurs in the uppermost spodic horizon regardless of the soils studied. Table 12 lists the clay content for each horizon.

The clay probably consists of sesquioxides and secondary clays formed from alteration products in the Al and A2 horizons as well as the uppermost spodic subhorizon.

The clay is probably held in place by the absorption of organic matter complexes, and kept from being eluviated to lower depths in the profile. Franzmeier (29) in his study of podzol soil formation concluded that there was synthesis of clays in Podzol B horizons from the allophane and other mineral components such as chlorite-like clays. Montmorillonite clay minerals (59) have been found to occur in the A2 horizons of many Podzols. This clay is evidently very resistant to further chemical breakdown and leaching in this intensely eluviated horizon. There is undoubtedly some eluviation of this clay into the upper spodic horizon where further transformation occurs when other elements are available for substitution into the clay crystal lattice.

Table 14, Appendix III, columns 1, 2, and 3 list percentages of extractable iron and aluminum by three extraction methods plus the total carbon content of each spodic horizon. Analysis of the data in the first three columns shows that there is very little difference between the oxalate and citrate-dithionite columns but a large difference in the pyrophosphate-dithionite column. While the oxalate figures are slightly higher than the citrate-dithionite figures for most of the spodic horizons, the pyrophosphate-dithionite figures are much higher for all of the horizons. The citrate-dithionite values from soils

having textures finer than sand or loamy sand are considerably higher than the oxalate values. The Onaway soil illustrates the relationship of extractants containing sodium dithionite with those that do not. Figure 5 shows the relationship of extractable iron contents to the clay content of an Onaway profile 21-2, with two extractants.

The last three columns of Table 14 list iron plus aluminum values for the three extraction methods plus the pyrophosphate-dithionite extractable carbon value. These columns were computed in order to use the present spodic horizon criteria.

Computer analysis of the data in Table 14 showed that there were close relationships between the various extractants, and whether total or extractable carbon was combined with the iron and aluminum contents obtained by the three extractants. Table 10 lists the correlations and equations of the curves. The oxalate extraction had the lowest coefficient of correlation, but this can be explained by the fact that the oxalate method extracted different forms of iron than the other methods did. The analysis also shows that the oxalate and citrate-dithionite extractions are fairly closely correlated (R = .932 and .961, respectively with the pyrophosphate-dithionite extractions.) even though different quantities and forms of iron and aluminum are extracted.

Correlation of the pyrophosphate-dithionite extraction method vs other extractants Table 10.

Extractant	Correlation Coefficient	Equation	When Pyro-dit. 2 = 1.0%, other extractants =
Oxalate 1*	0.895	Pyro-dit. $2 = .295 + .963$ 0xalate 1	.731%
Citdit. 1	0.931	Pyro-dit. 2 = .320 + .921 Citdit. 1	.739
Pyro-dit. 1	0.991	Pyro-dit. 2 = .052 + .874 Pyro-dit. 1	1.084
Oxalate 2**	0.932	Pyro-dit. $2 = .315 + 1.190$ 0xalate 2	.564
Citdit. 2	0.961	Pyro-dit. 2 = .398 + 1.100 Citdit. 2	.550
Pyro-dit. 2	1.000		

\* Total carbon by induction furnance.

\*\* Extractable carbon by pyrophosphate-dithionite extraction.

When total carbon is used instead of extractable carbon, the correlation coefficient for the pyrophosphate-dithionite values is 0.991. Even with the other extractants, and using total instead of extractable carbon, good correlations (R = .895 and .931) with the current criterion are evident. The criterion for amorphous materials for the other extractants is based on the current criterion. If the current criterion were ever to be changed then the equations would enable adjustments to be made for the other extraction methods also.

On the basis of the equations when the pyrophosphate-dithionite extractable iron, aluminum, and carbon equals 1.0%, which is the current criterion, then the following criteria are proposed for the other extractants.

Oxalate 1\* 0.8%

Cit. dit. 1\* 0.8

Pyro-dit. l\* 1.1

Oxalate 2\*\* .55

Cit.-dit. 2\*\* .55

\*Total carbon by induction furnace.

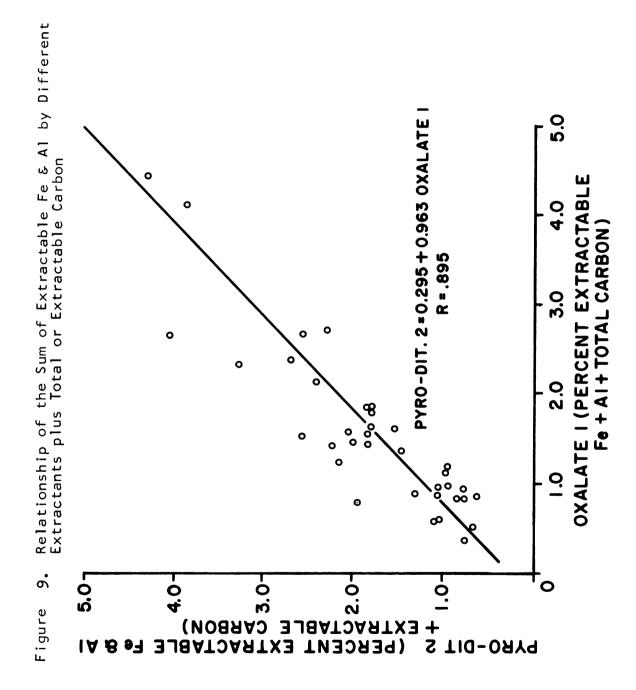
\*\*Extractable carbon by pyrophosphate-dithionite extraction.

Figure 9 shows the relationship between the current accepted extraction method and the oxalate extraction method using total rather than extractable carbon, and the pyrophosphate-dithionite method plus extractable carbon. The oxalate method was chosen because this extraction procedure appears to be more specific for extracting only the weathering products of soil development than the other extractants, and is also a simpler laboratory procedure.

Table 15, Appendix III, lists the ratios of extractable iron and aluminum plus either total or extractable carbon to the clay content of the sample for each of the three extraction methods. The soil horizons listed in Tables 14 and 15 of Appendix III, are those that contain the maximum amounts of extractable materials in each profile. Some of these layers are too near the surface to qualify as spodic horizons in plowed fields.

Table 16, Appendix III, shows the results of an experiment designed to test the 0.50% extractable iron value that has been proposed to separate Humods from Orthods. Both field moist and ignited moist hues from B and C horizons are listed.

Columns 2 and 3 list the moist hues of the Podzol B horizon of each soil before and after ignition. Column 4



indicates the amount of change in hue upon ignition of the B horizon. Columns 5 and 6 show the moist hues of the C horizon of each soil before and after ignition, while column 7 shows the amount of change in hue upon ignition. The data show that the reddening of the B horizon on ignition (column 4) occurs more frequently than if the ignited B is compared to the ignited C horizon (column 8). All but five of the C horizons tested reddened on ignition. By this criterion Rousseau, both Graylings, Minising 31-2, and Omega 52-1 also fail to show redder hues of the B than the C horizon after ignition. Apparently B horizons redder than 5YR after ignition would need to be included by this criterion, eg. Munising and Rousseau because of their reddish parent materials. Also, column 4 shows that there are only 4 cases where the B horizon fails to turn redder upon ignition when compared with the field moist hue. These soils are the Onaway 21-3, Kalkaska 24-1, and the two McBride profiles 43-1 and 67-1. The Onaway soils have more than 0.50% extractable iron, the McBride soils have less than 0.50% iron but more than 0.35%, and the Kalkaska B horizon has less than 0.35% extractable iron. The data thus shows that the soil texture affects the ignited hue with a given quantity of extractable iron. More extractable iron is needed in finer textured spodic horizons in order to have a change in hue upon ignition. Also, the valence or hydration state of the iron or its surficial distribution evidently can affect the ignited hues, as the Eastport 74-1 and the Oakville 50-1 soils illustrate. Both of these soils have low extractable iron contents in the B horizon, but have large changes in hue upon

ignition.

The use of a less than 0.18% exalate extractable iron content in the spodic horizon results in a fairly consistant separation of sandy spodic horizons that do or do not turn redder upon ignition. An analysis of the oxalate iron values with the proposed classification of the sandy soils show that those soils with iron contents of more than 0.18% are Orthods. All B horizons with less than 0.18% oxalate iron are either Humods or Udipsamments. Other criteria such as depth of the horizon, etc., eliminates the Udipsamments. A citrate-dithionite extractable iron value of 0.31% and a pyrophosphate-dithionite value of 0.25% make the same separations for sandy or loamy sand textured soils. For sandy loam-loam textured soils, the corresponding separations are at 0.48%, 0.81%, and 0.60% iron with the oxalate, citrate-dithionite and pyrophosphate-dithionite extraction methods respectively. In view of the wide differences between texture groups, the criterion needs to be different. The oxalate extractable iron content vs reddening on ignition compared to the ignited C horizon for comparison give less differences between textures than the pyrophosphate-dithionite or citrate-dithionite iron values. Another possibility then is to compare the extractable iron contents of B minus the C horizon.

this case the difference of B - C would be 0.20% for sands, and 0.37% for loams by the citrate-dithionite extraction procedure.

The following criteria are proposed based on these data and the ignition test results in Table 16, Appendix III, of spodic horizons that use oxalate, citrate-dithionite, and pyrophosphate-dithionite extractable iron and aluminum plus total carbon.

### Oxalate:

- 1. <u>Total % C. + oxalate Fe & Al</u> ≥ 0.12 % clay
- 2. Total % C. + oxalate Fe & Al  $\stackrel{.}{=}$  0.8
- 3. The spodic horizon or some subhorizon, should have less than 0.18% oxalate extractable Fe if sand or loamy sand, and less than 0.49% Fe if sandy loam or loam in order to quality as a Humod and iron content equal or greater than these amounts to qualify as an Orthod.

#### Citrate-dithionite:

1,2. The first two criteria above are 0.12 and 0.8% respectively, with the substitution of citratedithionite extractable iron and aluminum for the oxalate values. 3. The spodic horizon or some subhorizon should have less than 0.31% citrate-dithionite extractable iron if sand or loamy sand or less than 0.80% iron if a sandy loam or loam to qualify as a Humod and equal or greater amounts in order to qualify as an Orthod.

## Pyrophosphate-dithionite:

The criteria using extractable carbon are unchanged.

The criteria using total rather than extractable carbon

are as follows:

- 1. Total % C. + Pyrophosphate-dithionite Fe & Al ≥ 0.18 % clay
- 2. Total % C. + Pyrophosphate-dithionite Fe & Al ≥ 1.1%
- 3. The spodic horizon or some subhorizon should have less than 0.25% Pyrophosphate-dithionite Fe if a sand or loamy sand or less than 0.60% Fe if a sandy loam or loam in order to qualify as a Humod, and equal or greater amounts to qualify as an Orthod.

A Typic Haplohumod must have >1% OM(0.58% C) in the upper 12 inches of the B horizon, while Typic Haplorthods must have >2% OM(1.16% C) in the upper 4 inches of the B horizon.

Table 17 classifies the soils according to the proposed revised criteria for recognizing a spodic horizon, as well as the classification according to the present criteria. The Quick Test colors, discussed earlier, are shown as the last column in this Table to illustrate that this test usually separates the Humods and Orthods from the Udipsamments. A soil series name in parenthesis in the first column is the proposed correlation if different from the earlier name, and the subgroup name in parentheses in the last column is the proposed subgroup name according to the January 1968 listing. These commonly differ from the placements based on these data.

These data and revised criteria along with Franzmeier's and Messenger's data, contained in Tables 18 and 19 respectively, throw grave dbout on the separation of soils in the field on the basis of the parent material hue.

The Rubicon B-l profile (Table 19) has developed in 10YR hue parent material and was formerly classified as a Spodic Udipsamment. By the revised criteria it is an Entic Haplorthod. The Rubicon C-l profile has developed in 7.5YR hue parent material, and is classified as an Entic Haplorthod as it had been earlier. Both the C-2 and D-l profiles were formerly called Kalkaska, but were

developed in 7.5YR hue parent materials characteristic of Hiawatha. The C-2 profile is now classified as a Typic Haplorthod and should be correlated with the Hiawatha series, while the D-1 profile is an Entic Haplorthod and should remain as Kalkaska.

In conclusion, the hue of the parent material has been used as a clue in determining the classification of sandy Spodosols in Michigan. The hue of the parent material is apparently related to the quantity and kinds of dark minerals that are present and available for chemical weathering in the course of soil development. Sandy soils developing in 7.5YR and redder hue parent materials commonly qualify as Typic Haplorthods where they have well developed spodic horizons, and those developing in 10YR hue parent materials commonly qualify as Entic Haplorthods or as Spodic Udipsamments. However, the chemical composition of the spodic horizon or mineralogy of the profile, may be better criteria for differentiating these soils.

# C. Classification and Correlation of Soils Studied

Table 17 shows the classification of the soils that were used in this study in the Comprehensive Soil Classification System. The Rubicon 2-1 soil from the upper

peninsula has developed in 7.5YR hue parent material. It is proposed that this Rubicon profile be combined with the Vilas which also has reddish hue parent material. The Rousseau 7-4 profile was supposed to have been a Vilas site but the high fine sand content of the profile put the soil into the Rousseau series rather than the The Rousseau profile, while characteristic of the upper peninsula variety, may not be representative of the southern Michigan variety which has developed in yellowish hue IOYR parent materials. By present criteria it is an Entic Haplohumod. The Omega and Grayling profiles while having developed in both reddish (Omega) and yellowish (Grayling) parent materials show very little difference in carbon, iron or aluminum contents of the Podzol B horizons. These soils were both formerly classified as Brown Podzolic soils. On the basis of the data and lack of sufficient A2 horizons, they are both now classified as Typic Udipsamments. However, the Omega is borderline to an Entic Haplorthod since its upper B horizon extends to a depth of 8 inches, and contains nearly enough carbon, iron and aluminum to qualify for a spodic horizon. Further, its B horizon when ignited, is/redder than its ignited C horizon. This is not true of Grayling. It is recommended that these two series be kept separate.

The Rubicon 16-2 profile is more characteristic of the series that has developed in yellowish 10YR hue parent material and is classified as an Entic Haplohumod. On the basis of the chemical data, there is commonly enough difference in the amorphous materials in the B horizons of the soils developed in sand 7.5YR and 10YR hue parent materials to justify their separation. It is proposed here that the Rubicon developed in 10YR hue parent material containing fewer dark minerals be classified as Rubicon, and the similar soils commonly developed in 7.5YR hue parent material and classifying as Entic Haplorthods be recognized as Vilas. The Vilas soils contain more than 0.18% oxalate extractable iron in the B horizon while the Rubicon soils do not. The Rubicon 16-2 is an Entic Haplohumod, the Rousseau 7-4, and Vilas 7-2 are Entic Haplorthods.

The Onaway and McBride soils were included in this study because it was felt that these soils might not qualify as Spodosols. They both do, but just! They are both near the borderline for the ratio of extractable iron and aluminum plus either total or extractable carbon/clay to qualify as having spodic horizons (Table 15, Appendix III).

The Oakville and Eastport soils were included in order to determine if these podzol-like sandy soils might have sufficient quantities of iron and aluminum without the dark B horizon color to qualify as spodic horizons.

It is proposed here that the Eastport be classified as a Spodic Udipsamment because of the presence of an A2 horizon, and Oakville as a Typic Udipsamment since it may have or not have an A2 horizon and since its upper B horizon does not extend below 7 inches. Only by the revised citrate-dithionite and pyrophosphate-dithionite with total carbon requirements, does it have enough amorphous materials to qualify as a spodic horizon.

Table 18, Appendix III, lists the soils used by
Franzmeier (29) in his study of Podzol formation. The
data have been transformed so that they can be used in the
revised spodic horizon criteria. All of the soils were
sampled in northern lower Michigan. The soil series name
in parentheses is the proposed correlation of any particular
soil if different from the name under which it was sampled.
The Rubicon represents the weak side of the series as
evident by the light colored B horizon and low extractable
materials. It probably should be correlated as Deer Park
a Spodic Udipsamment. The Kalkaska soil readily fits into
the Entic Haplohumods. The Blue Lake soils fit into the

Alfic Haplorthods or Alfic Haplohumods, with the presence of thin argillic horizons below the spodic horizon. However, the criteria throw a soil out of the Typic Haplohumods if it possesses an argillic horizon, even if the iron content is low. Consequently, a new subgroup of Alfic Haplohumods should be proposed, or these soils should be included with the Alfic Haplorthods as suggested in Tables 17 and 18.

Table 19 lists the solls and chemical data from Messenger's Ph.D. thesis. All of the soils were sampled in the Upper Peninsula in Delta and Schoolcraft Counties. The classification and correlation of the soils in Table 19 is covered in an earlier section.

One of the major purposes of this study besides testing the spodic horizon criteria was to determine if there were any and enough significant differences between the Kalkaska and Hiawatha soils to justify keeping them separate. The Hiawatha soils are developing in reddish 7.5-5YR hue parent materials, while the Kalkaska soils are developing in yellowish 10YR hue parent materials. The problem of classification and correlation arose in Delta County in the Upper Pensinula, where both yellowish and reddish parent materials occur. The source of the parent material and the related glacial geology are very important criteria

in the field recognition and separation of these soils. The problem occurred when the reddish and yellowish parent materials were mixed together or occurred together in a complex pattern in the landscape. On the basis of the laboratory data, there are very distinct differences between the two soils. Hiawatha is classified as a Typic Haplorthod or Typic Haplohumod in Table 17, while the Kalkaska is classified as an Entic Haplorthod or Entic Haplohumod. The revised criteria place both soils in the Orthods. On the basis of this classification, it is proposed that the Kalkaska mapped in 7.5YR or redder hue parent material as in Delta County be correlated to Hiawatha, and the other Kalkaska mapped in 10YR hue parent materials with the associated mineralogical and chemical profile differences be correlated as Kalkaska.

The separation between these two soils will be geographic in nature and dependent on the glacial geology of the area and probably also associated climatic and vegetative differences. Thus greater emphasis must be placed on the glacial geological aspects of a soil survey area when both soils are mapped in it. Knowledge of the glacial geology can help the soil mapper make the best separations of the soils. However, in areas of mixed parent materials, chemical analysis may be necessary before

a decision is reached on how the area is to be mapped and correlated. Complexes or undifferentiated units of the two may be necessary in some cases.

Canadian Classification of Podzolic Soils

Appendix IV contains the classification criteria used in Canada in their soil classification system. Table 12 compares the U.S. and Canadian classification systems for the soils in this study. The U.S. system separates the 12 soil series into 6 groups. The Canadian system does the same but with different groupings. The requirements for a soil to qualify with a Podzol B horizon (Bf or Bh) are much more restrictive in the Canadian system. Entic Haplorthods and Spodic Udipsamments are grouped together in the Canadian system, while only the Hiawatha series qualifies as an Orthic Podzol and possesses a Bf The Munising soils also have a Bf horizon and are classified as Bisequa Podzols. Table 20 in Appendix IV contains the interpretation of the data on the Michigan The table lists the kind of B horizon and the soils. placement of the soils into the Canadian Soil Classification System.

Table 11. Comparison of soil placements in the U.S. and Canadian soil classification systems

Soil	Profile	U.S. Classifi-	Canadian Classifi-
<u></u>	No.	cation (March 1967)	cation*
Rubicon	2 - 1	Entic Haplohumod	Arenic Podzo Regosol
Munising	7-1	Alfic Fragiorthods	Bisequa Podzol
Vilas	7-2	Entic Haplohumod	Arenic Podzo Regosol
Omega	7-3	Typic Udipsamment	Degraded Acid Brown Wooded
Rousseau	7-4	Entic Haplohumod	Arenic Podzo Regosol
Grayling	16-1	Typic Udipsamment	Degraded Acid Brown Wooded
Rubicon	16-2	Entic Haplohumod	Arenic Podzo Regosol
Grayling	21-1	Typic Udipsamment	Degraded Acid Brown Wooded
Onawa y	21-2	Alfic Haplorthod	Bisequa Gray Wooded
Onawa y	21-3	Alfic Haplorthod	Bisequa Gray Wooded
Ka 1 kaska	24-1	Entic Haplohumod	Arenic Podzo Regosol
Hiawatha	31-1	Typic Haplorthod	Orthic Podzol
Munising	31-2	Alfic Fragiorthod	Bisequa Podzol
Hiawatha	31-3	Typic Haplohumod	Orthic Podzol
McBride	43 - 1	Alfic Fragihumod	Bisequa Gray Wooded
Oakville ·	50-1	Typic Udipsamment	Orthic Acid Brown Wooded

Table II, continued

Soil	Profile No.	U.S. Classifi- cation	Canadian Classifi- cation*
0mega	52-1	Typic Udipsamment	Degraded Acid Brown Wooded
McBride	67-1	Alfic Fragihumod	Bisequa Gray Wooded
Ka 1 kas ka	67-2	Entic Haplorthod	Arenic Podzo Regosol
Eastport	74-1	Spodic Udipsamment	Arenic Podzo Regosol

<sup>\*</sup>The Canadian Classification System requirements are contained in Appendix IV.

## D. Discussion and Research Needs

Spodosols are complex soils. Where the podzolization process acts with greatest intensity the effects are easy But, chemically, there is still much to be learned about how these properties develop and the magnitude and significance of the differences. For example, how sesquioxides are made soluble, transported, and redeposited is still not clear. It is well established that soil organic matter is associated with much of what occurs during spodosol formation. Investigators have reported that two organic acids or groups of acids having specific solubilities and characteristics, fulvic and humic acid groups are the agents involved. Some evidence is presented that shows humic acids to be the major constituent of the organic matter of the spodic horizon, but other evidence shows fulvic acids to be the major constituent of spodic horizons. Fulvic acid is the more soluble of the two acids and is thought to be the agent responsible for solubilizing and chelating iron and aluminum and transporting these metals to lower positions in the profile. Humic acids occur primarily in the surface horizons and to a lesser extent in the spodic horizon.

Undoubtedly, there are several kinds of spodic horizons. The nature of the organic matter in them is dependent at least in part on the natural vegetation and the pH of the soil. Also, the nature of the extractant used to remove the organic matter from spodic horizons can influence the amounts of fulvic and humic acids that are removed. Investigations in identifying the components of fulvic acid show that polyphenol structures occur in large quantities, and readily complex with iron and aluminum.

Research (82) on the factors that cause the precipitation of the mobile organic matter-sesquioxides has shown that aluminum ions as well as iron ions are probably among the major precipitators. Calcium and magnesium ions, when they occur, also readily cause precipitation. In fact, in soils developing from calcareous parent materials or those with high base status, calcium and magnesium may be the only ions available that can cause precipitation of the iron and aluminum compounds. Later after the bases have been leached out, and leaching has produced quantities of free aluminum, and iron ions, these may take over the role of precipitator.

The laboratory data presented in this paper shows that often extractable aluminum maxima occur lower in the

profile than the carbon and iron maxima which generally occur together. The calcium and magnesium ions, if present, are associated with the carbon maxima which occur in the uppermost part of the spodic horizon. What agent is responsible then for the precipitation of aluminum when there are no detectable amounts of bases in the horizon below? Evidently, slight changes in pH cause the precipitation of aluminum in acid parent materials. The results of this study appear to substantiate other research (82). However, the lower horizons of the Onaway and Eastport soils contain quantities of calcium, so the pH probably doesnot affect precipitation but the calcium ions are the agent responsible. That there are differences in spodic horizons can be readily seen, by comparing the Onaway (21-3) data with the Munising (31-2) data. This particular Onaway profile has no pH in  $H_2O$  below 7.0 in any horizon. How then can a spodic horizon develop in a soil this high in pH? The aluminum maximum occurs below the iron and carbon maxima. In the case of this soil the composition of the organic matter resulting from the natural vegetation must be the agent responsible for the mobilization, transportation and redeposition of the sesquioxides. Populus tremuloids which grows naturally on the Onaway soils has been shown to contain large amounts of polyphenols

in the leaves. The polyphenols apparently are able to complex iron and aluminum even at high pH. How the sesquioxides are concentrated in one particular horizon is not known. Perhaps the higher clay content in the horizon below the spodic horizon is the cause for the precipitation in the horizon above? The Munising profile, on the other hand, represents the more classic aspects of spodic horizon development, along with other soils that sustained a mixed conifer-hardwood forest vegetation since soil development began. Conifer vegetation has been shown to contain low amounts of polyphenols, with the exception of hemlock (Tsuga canadensis). Hemlock moves in on sands only after soil development has progressed to a point where the soil is capable of supporting stands of hemlock. After hemlock invades a pine stand or hardwoods, the podzolization process intensity increases due to the larger quantities of polyphenols available to transport iron and aluminum compounds to lower positions in the profile.

Many methods have been proposed and used to extract iron and aluminum from soil horizons, but none have been designed specifically for spodic horizons. The procedures

utilizing sodium dithionite remove too much iron from spodic horizons. The acid ammonium oxalate extraction procedure done in darkness extracts only the amorphous forms of iron from spodic horizons. This extraction method appears at this time to be the most suitable for the extraction of spodic horizons. It has been proposed that the amorphous iron and aluminum compounds that occur in spodic horizons are due to soil forming processes. If so, to determine the amorphous materials would be a way of determining the degree of podzolization or the intensity of the process.

The oxalate extraction procedure has several advantages over the other methods that were tested and compared in this paper. They are: 1. simplicity, 2; ease of operation, 3. use of time efficiently during the extraction period, 4. ability to selectively remove only amorphous iron alteration products.

Many methods have been devised to analyze for organic carbon, iron and aluminum contents of soils. The Leco carbon analyzer utilizing a high temperature induction furnace and others like it are taking the drudgery out of analyzing soils for their carbon content. The Leco analyzer will determine the carbon content of a sample every 2 minutes. The other dry and wet combustion methods require considerable time if much accuracy is required.

The fast dry and wet combustion methods are also quite inaccurate. The use of atomic absorption spectroscopy is a superior, faster and more accurate method of analyzing for iron and aluminum than the colorimetric methods now in common use. From 400 to 600 samples can be analyzed per day using a Perkin-Elmer 303 for example.

The use of rapid and accurate analytical procedures enables tests to be made of how reproducible an extraction procedure or analytical method is. Very little data has ever been reported anywhere that shows how reproducible an extraction procedure is. This is because of the time required to analyze the many samples and replicates necessary using the slow colorimetric analytical methods. What is usually shown is that a procedure can remove more or less iron from a given soil sample than another procedure.

### IV. SUMMARY AND CONCLUSIONS

The soils in this study were classified according to both the current classification criteria as well as some new proposed criteria. The current criterion for the extractable iron (.5%) which separates the Orthods from the Humods needs to be changed. Lowering the extractable iron requirements for sands to .18%, .31%, and .25% for sands for the oxalate, citrate-dithionite, and pyrophosphate-dithionite procedures respectively, the changing the requirement to .49%, .80%, and .60% for loamy soils for the oxalate, citrate-dithionite, and pyrophosphatedithionite methods respectively would bring the soils with these extractable Fe contents more in line with the "redder on ignition" criterion. This proposed change would put more of the sands into the Orthods (Rubicon 2-1, Vilas 7-2, Rousseau 7-4, Kalkaska 24-1, and Hiawatha 31-3) which according to the current criterion, have insufficient extractable iron to qualify for Orthods. The reddening on ignition test shows that the .5% iron criterion be changed to the values shown above.

either the Typic or Entic Haplohumods. By the proposed Fe contents criteria only 5 profiles fit into the Humods, but 3 of these profiles fit into subgroups not yet recognized. The current criteria also split up some of the paired soil profiles. For example, the 2 Hiawatha and 2 Kalkaska profiles are split into 4 different subgroups. The proposed criteria place the two Hiawatha profiles together and the two Kalkaska profiles together. Even with the proposed Fe criteria, the placement of profiles of the same series do not always agree with each other. For example, one of the Onaway profiles would be an Orthod and the other a Humod. Both would be Alfic Haplorthods, however, if Humods are not allowed to have argillic horizons. If the requirement stands that Humods have no argillic horizon, then The McBride series would be placed into the same subgroup as the Munising series but would be separated at the series level because of differences in pH, acid vs calcareous parent material and degree of spodic horizon development, or put into a new subgroup.

It is proposed here to eliminate soils having spodic horizons that meet the requirements for the Humods but having a fragipan and an argillic horizon, by creating a new subgroup in the Fragiorthods. The new subgroup would be the Alfentic Fragiorthods. This change would put the McBride series into the Alfentic Fragiorthods and separated from the Munising series at a higher level than the series level. This proposed subgroup would have the requirement that the spodic horizon does not meet the requirements for a Typic Fragiorthod spodic horizon but has a weak fragipan and an argillic horizon.

The new criteria are summarized below for the identification of spodic horizons that use oxalate or citratedithionite extractable iron and aluminum plus total carbon or pyrophosphate-dithionite extractable iron and aluminum plus total carbon rather than extractable carbon.

### Oxalate:

- 2. Total % C. + Oxalate Fe & Al ≥ 0.8%
- 3. The spodic horizon or some subhorizon should have less than 0.18% exalate extractable Fe if a sand and less than 0.49% Fe if a loam to qualify as a Humod and iron content equal or greater than these amounts to qualify as an Orthod.

### Citrate-dithionite:

- 1 & 2. The first two criteria above, 0.12 and 0.8 respectively with the substitution of citrate-dithionite extractable iron and aluminum for oxalate iron and aluminum.
- 3. The spodic horizon or some subhorizon should have less than 0.31% citrate-dithionite extractable iron if a sand and less than 0.80% Fe if a loam in order to qualify as a Humod, and equal or greater amounts of Fe to qualify as an Orthod.

# Pyrophosphate-dithionite:

- 1. <u>Total % C + Pyro-dit. Fe & Al</u> ≥ 0.18 % clay
- 2. Total % C + Pyro-dit. Fe & Al ≟ 1.1%
- 3. The spodic horizon or some subhorizon should have less than 0.60% pyro-dit Fe if a sand or less than 0.60% Fe if a loam to qualify as a Humod, and equal or greater amounts to qualify as an Orthod.

The criteria where pyro-dit extractable carbon is required are unchanged and would be =0.15 and =1.0% in 1 and 2 above.

Table 17 in Appendix III summarizes the current and proposed classification of the soils in this study.

The Quick Test very effectively sorts out the Haplorthods from the Udipsamments and even the Entic subgroup. It also sorts out the Humods from other soils but not from the Orthods. In summary, the Quick Test helps to determine whether a soil has a spodic horizon with a minimum amount of laboratory analysis. Further field testing is necessary to determine how effective the Quick Test is when both the air and soil temperatures are low. The temperature limits of about 65-70°F, appears to be the minimum at this time. On the basis of the data Munsell colors of 7/3 or values of 7 or less and chromas of 3 or more all qualify B horizons as a spodic horizon. Values of 8 or more and chromas of 2 or less (8/1 or 8/2) sort out soils as not having spodic horizons. Munsell color notations of 7/1 and 7/2 are borderline and place the soils into either the Spodic Udipsamments, Entic Haplorthods, or the Entic Haplohumods. Careful control of temperatures and soil amounts, it seems, may eliminate this uncertainty. The Quick Test procedure is simple and can be done while writing a profile description in the field. More data is needed on other soils, particularly less well drained Spodosols.

The soils that were used in this study generally represented both the strong and weak ranges of the Spodosols

as recognized today in Michigan. The data in this paper should pertain generally to the particular soil series wherever mapped.

With faster and easier extraction procedures and analytical methods it is possible that many more soils will be characterized with complete physical and chemical data. Spodosols especially require chemical data for the proper classification into subgroups.

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APPENDIX I. Spodosol
Classification Criteria
in the United States

#### SUMMARY OF THE LIMITS OF THE SPODIC HORIZON

- If there is an albic horizon thicker than 18 cm
   inches) or there is an intermittent albic horizon below an Ap horizon, a spodic horizon has:
  - a. Enough amorphous material that:

# percent extractable C + Fe + Al ≥ .15 percent clay

- b. A thickness of 1 cm or more, either as a continuous horizon or as a sum of lamellae within 1 m (40 inches).
- c. Extractable carbon + iron + aluminum \( \rightarrow \) 1.0

  percent or moist color hues are 7.5YR or redder and moist values of 3 or less in some continuous part of the horizon or in any one subhorizon that is at least 1 cm thick and hues are as red or redder than the underlying horizon.
- 2. If an 0, Ap, or an Al rests on the spodic horizon the spodic horizon has the requirements of 1. above, and in addition has:
  - a. A 15 bar water content of less than 20%;
- b. Enough depth that the horizon is not obliterated by plowing to 18 cm (7 inches) or enough degree of expression that the horizon after mixing to 18 cm meets the criteria listed under 3.

As none of the soils used in this study qualified for the rest of the criteria listed in the spodic horizon section, the remainder of the summary of requirements is not listed here.

After a soil is found to possess a spodic horizon, they may be fitted into the classification of the Spodosols in the Comprehensive Class system. Following is the summary of the requirements of the possibilities that the soils might fit into:

## Humods. Spodosols that -

- are never saturated with water, or do not have the characteristics associated with wetness as defined for Aquods;
- 2. have one or both of:
- a. in 50 percent or more of each pedon a spodic horizon with a subhorizon that contains dispersed organic matter and aluminum and that lacks sufficient free iron to turn redder on ignition (less than 0.50% in the fine earth fraction expressed as Fe).
- b. an Ap horizon that has a moist value of 3 or less and a moist chroma of 2 or less and that rests directly on a spodic horizon having in its upper part a subhorizon or some tongues possessing one or both of:

- (1) dispersed organic matter and a moist chroma of 3 or less;
- (2) less than 0.7% free iron expressed as Fe.

## Haplohumods

- have soil temperatures warmer than those of Cryohumods, and have mean summer and mean winter soil temperatures of 50 cm (20 inches) that differ by 5 C. or more;
- 2. have no fragipan.

# Typic Haplohumods. Haplohumods that:

- a. have either:
  - (1) a spodic horizon that has 1% or more organic matter (0.58% carbon) in the matrix of the first 30 cm (12 inches) below the top of the spodic horizon, or
  - (2) an upper subhorizon of the spodic horizon that has 5% or more organic matter (2.9% carbon) in the upper 2 cm that is continuous or is present in more than 90 percent of the area of each pedon;
- b. have no argillic horizon;

  <u>Entic Haplohumods</u>. Haplohumods like the Typic except for a.

# Orthods. Spodosols that

- have a spodic horizon that has in some subhorizon a ratio of free iron (elemental) to carbon, by percentage, of 6 or less;
- 2. have one of the following:
  - a. an Ap horizon that has a moist value of more than 3 or a moist chroma of more than 2 and that rests directly on a spodic horizon;
  - b. an Ap horizon that rests directly on a spodic horizon and the spodic horizon has in all parts moist values and chromas of more than 3 or has 0.7% or more free iron (elemental) in all parts;
  - c. a spodic horizon that <u>lacks</u>, or has in less than 50% of each pedon, any subhorizon that contains dispersed organic matter and aluminum (and that <u>lacks</u>) sufficient free iron to turn redder on ignition (less than 0.50% in the fine earth fraction expressed as Fe)
- are never saturated with water or lack the characteristics associated with wetness of Aquods.

### Fragiorthods. Orthods that

- 1. have a fragipan below the spodic horizon;
- Typic Fragiorthods. Fragiorthods that
  - a. have no argillic horizon underlying the spodic horizon;
  - b. have no distinct or prominent mottles in the spodic horizon;
  - c. have a continuous spodic horizon that is very firm when moist (ortstein), or that is more than 10 cm thick and has 2% or more organic matter (1.16% carbon) in the upper 10 cm;
  - d. have temperatures warmer than those of Cryorthods.
  - e. have no intermittent upper subhorizon that has coatings of dispersed organic matter and that lacks sufficient free iron to turn redder on ignition (less than 0.35% in the fine earth fraction expressed as Fe); if plowed and the Ap horizon rests directly on the spodic horizon, there are no tongues of such a subhorizon;
  - f. if plowed, and the upper part of the spodic horizon is thus mixed in the Ap (lacks a continuous albic horizon), has more than 2% organic matter (1.16% carbon) in the Ap horizon;

Alfic Fragiorthods. Fragiorthods like the typic except for (a) have base saturation of 35% or more in some part of the argillic horizon, or have an albic horizon that tongues into the argillic horizon or that have a mean annual soil temperature of less than 8 C. (47 F.).

## Haplorthods. Orthods that

- have soil temperatures warmer than those of Cryoorthods, and have mean summer and mean winter temperatures at 50 cm that differ by 5 C or more;
- 2. have no fragipan;

## Typic Haplorthods. Haplorthods that

- a. have no argillic horizon below the spodic horizon;
- b. have a continuous spodic horizon that is very firm or extremely firm when moist (ortstein) or that is more than 10 cm thick and has at least 2% organic matter (1.16% carbon) in the upper 10 cm;
- c. have no distinct or prominent mottles of approximate spherical shape in the spodic horizon unless the variability in color is associated with differences in consistence in such a manner that the redder or darker portions are extremely firm or very firm;

- d. have no chromas of 2 or less with mottles, or chromas of less than 2 without mottles, that are dominant in the matrix within 15 cm (6 inches) of the base of the spodic horizon but within 1 m (40 inches) of the surface of the soil;
- e. have no horizon 15 cm (6 inches) or more thick below the spodic horizon but within 1 meter (40 inches) of the surface that has a brittle matrix when wet and contains some durinodes;
- f. have no lithic contact within 50 cm of the surface;
- g. have <u>no</u> intermittent upper spodic subhorizon that has coatings of dispersed organic matter and that lacks sufficient free iron to turn redder on ignition (less than 0.50% in the fine earth fraction expressed as Fe);
- h. have less than 10% organic matter (5.8% organic carbon) in the upper 10 cm (4 inches) of the spodic horizon;
- i. have 2% or more organic matter (1.16% organic carbon) in the Ap horizon if the disturbed layer extends into the upper part of the spodic horizon.

- Alfic Haplorthods. Haplorthods like the typic except for a and b and the argillic horizon either contains tongues of an albic horizon, or has base saturation of 35% or more in some part, or has a mean annual soil temperature of less than 8° C.
- Entic Haplorthods. Haplorthods like the typic except for b,
   because of thickness or low organic matter content.
- <u>Humic Haplorthods</u>. Haplorthods like the typic except for g or h.

Note: This is an abbreviated key of the Spodosol classification that is found in the Comprehensive System of Soil Classification Supplement, 1967. It applies to the soils in this study.

The following chart is an abbreviated version of the Entisol classification from the Comprehensive Soil Classification System (revised March 1967).

# **Entisols:**

Mineral soils that have no diagnostic horizon other than an ochric or an anthropic epipedon, an albic or an agric horizon.

#### Psamments. Entisols that

- have below the Ap horizon or 25 cm, whichever is deeper, textures of loamy fine sand or coarser in all parts either to a depth of 1 m or to a lithic or a paralithic contact, whichever is shallower;
- 2. have no fragments of diagnostic horizons that can be identified and that occur more or less without discernable order in the soil below any Ap horizon but within the series control section.
- 3. are not permanently saturated with water and lack the characteristics associated with wetness defined for Aquents.

# Udipsamments. Psamments that

- have soil temperatures warmer than those of Cryopsamments and mean summer and mean winter soil temperatures at 50 cm that differ by 5° C., or more;
- 2. are not dry in all subhorizons between 18 and 50 cm or a lithic or a paralithic contact shallower than 18 cm in more than 7 out of 10 years for as much as 60 consecutive days, and are not dry in some subhorizon between these depths for as much as 90 cumulative days in most years;

3. have in the sand fraction, less than 95 percent quartz, zircon, tourmaline, rutile, or other normally insoluble minerals that do not weather to liberate iron or aluminum.

## Typic Udipsamments. Udipsamments that

- a. have no lamellae within 1.5 m of the soil surface that meet all the requirements for an argillic horizon except thickness;
- b. have no mottles with chromas of 2 or lessto a depth of 1 m;
- c. have no lithic contact within a depth of 50 cm;
- d. have no albic horizon that is underlain by a horizon having stronger color values 1 unit or more darker.

<u>Spodic Udipsamments</u>. Udipsamments like the typic except for d.

APPENDIX II.

Profile Descriptions of Soils Studied

#### Rubicon Sand

Location: Alger County, Michigan. NE1/4, NE1/4 section 1, T45N, R19W. 1/8 mile south of USFS Road 2264

T45N, R19W. 1/8 mile south of USFS Road 2264 on USFS Hy 13; 300' west from road into woods.

<u>Vegetation</u>: Red Pine, few Aspen; ground cover primarily

Bracken Fern.

Parent Material: Sand

<u>Slope</u>: 1%

Physiography: Outwash Plain.

Drainage: Well Drained.

Collectors: D. P. Franzmeier; E. P. Whiteside, D. A. Lietzke

and R. W. Johnson.

Description By: Whiteside and Johnson.

<u>Horizon</u>	<u>Depth</u>	Description
A 1 2 - 1 - 1	0-2-1/2"	Dark gray (10YR4/1 dry) and black (10YR2/1 moist); sand; weak fine granular structure; very friable; very strongly acid; abrupt smooth boundary.
A 2 2 - 1 - 2	1-1/2-4"	Light brownish gray (10YR6/2 dry) and brown to dark brown (7.5YR 5/2-4/2 moist); sand; weak coarse granular to weak medium subangular blocky structure; very friable; very strongly acid; abrupt wavy boundary.
B21ir 2-1-3	4-9"	Brown (7.5YR5/4 dry) and reddish brown to dark reddish brown (5YR 3/4-4/4 moist); sand; weak coarse subangular blocky structure; very friable; very strongly acid; gradual smooth boundary.

<u>Horizon</u>	<u>Depth</u>	Description
B22ir 2-1-4	9-14"	Brown to strong brown (7.5YR 5/4-5/6 dry) and brown to dark brown (7.5YR4/4 moist); sand; weak coarse granular to weak medium subangular blocky structure; very friable; few chunks of weak to strongly cemented ortstein; medium acid; gradual smooth boundary.
B31 2-1-5	14-21"	Strong brown to reddish yellow (y.5YR5/6-6/6 dry) and brown (7.5YR5/4 moist); sand; single grain loose; few massive chunks of weakly tostrongly cemented ortstein; medium acid; abrupt smooth boundary.
B32 2-1-6	21-27"	Brown (7.5YR5/4); sand; single grain; loose; few massive chunks of weakly to strongly cemented ortstein; medium acid; abrupt smooth boundary.
C1 2-1-7	27-40"	Light brown (7.5YR6/4); sand; single grain; loose; medium acid; abrupt smooth boundary.
C2 2-1-8	40-65"	Light brown (7.5YR6/4); sand with a small proportion of coarse sand and fine gravel; single grain; loose; slightly acid; abruptsmooth boundary.
C3 2-1-9	65-102"	Light brown (7.5YR6/4) to light yellowish brown (10YR6/4); sand; single grain; loose; slightly acid.
Ortstein* 2-1-10	9-27"	Brown to dark brown (7.5YR4/4) and dark reddish brown (5YR3/2) in approximately equal proportions; sand; massive; weakly to strongly cemented; chunks or tongues are 1-1/2-3" wide and 10-18" thick; roots follow the outside of the ortstein tongues, however, only a few penetrate the mass; strongly acid.

<sup>\*</sup>Occurs in the lower part of the B22ir, B31, and the upper part of the B32 horizons. Represents approximately 10% of the pit surface area sample.

#### Munising Loamy Sand

Baraga County, Michigan. SW1/4, NE1/4, Sec. 4, T51N, R31W, 0.6 miles NE of the Ravine River and  $150^{\circ}$  south of the road. Location:

Vegetation: Hard Maple and Yellow Birch.

Parent Material: Sandy Loam glacial till.

<u>Slope</u>: 4-5% north, on a complex slope.

Physiography: Moraine.

<u>Drainage</u>: Well drained.

D. Franzmeier, E. P. Whiteside, D. Lietzke,

R. Johnson, 7/26/66.

Description By: R. Johnson and E. P. Whiteside

<u>Horizon</u>	<u>Depth</u>	<u>Description</u>
A1 7-1-1	0-1"	Black (5YR2/1); loamy sand-sandy loam; weak fine granular structure; friable; strongly acid; abrupt smooth boundary.
A 2 7 - 1 - 2	1-9"	Pinkish gray (5YR6/2 moist) and light gray (5YR6/1 dry); loamy sand; massive; slightly hard when dry; very strongly acid; abrupt wavy boundary. (few tongues extend into the B21 horizon).
B21hir 7-1-3	9-13"	Dark reddish brown (5YR3/3-3/2 moist) and dark reddish brown (5YR3/3 dry); fine sandy loam; weak very coarse granular to weak medium subangular blocky structure; friable with strongly cemented tongues; very strongly acid; clear wavy boundary.

<u>Horizon</u>	Depth	Description
B22ir 7-1-4	13-21"	Reddish brown (5YR4/3 moist) and reddish brown (5YR4/4 dry); fine sandy loam; weak coarse subangular blocky structure; slightly hard when dry, and friable when moist; strongly acid; clear wavy boundary.
B3x 7-1-5	21-29"	Reddish brown (2.5YR4/4 moist) and reddish brown (2.5YR5/4 dry); loamy sand; weak thick platy structure to massive; slightly hard and brittle when dry; medium acid; clear wavy boundary.
A'2× 7-1-6	29-40"	Pinkish gray (5YR6/2) loamy sand with reddish brown (2.5YR4/4) chunks which appear to be remants of the B; massive; vesicular; very hard and compact when dry; brittle; strongly acid; abrupt irregular boundary.
B'2x 7-1-7	40-48"	Reddish brown (2.5YR4/4) sandy loam, with pinkish gray (5YR6/2) tongues up to 2" thick extending down from the A'2x; thin clay flows in root channels; massive; vesicular; very hard and brittle when dry; very compact; very strongly acid; clear wavy boundary.
B'22t 7-1-8	48-62"	Reddish brown (2.5YR4/4); sandy loam; with clay flows along vertical ped faces, in root channels and in pores; massive; friable; very strongly acid; gradual wavy boundary.
C1 7-1-9	62-82"	Reddish brown (2.5YR4/4) to weak red 2.5YR4/2); sandy loam; massive; friable; medium acid; gradual wavy boundary.

<u>Horizon</u>	<u>Depth</u>	Description
C2 7-1-10	82-100"	Reddish brown (2.5YR4/4) to dusky red (10R3/4); sandy loam; massive; friable; slightly acid.

Note: Colors given refer to moist conditions unless otherwise stated

Roots are concentrated in the upper 20-24" with a few in the A2. Roots extend to depths of 54" along tongues of A'2.

#### Vilas Sand

Baraga County, Michigan. SW1/4, NW1/4, Sec. 8, T49N, R34W. 0.6 miles north of the Big Lake landing field, and 16 paces east of the road. Location:

Oak, Large Tooth Aspen, White Birch, Red Maple, Vegetation:

and Jack Pine. Ground cover of Sweet Fern, Bracken Fern, Blueberries, and Wintergreen.

Parent Material: Sand.

Slope: 0-1%

Physiography: Outwash Plain.

Drainage: Well Drained.

<u>Collectors</u>: D. Franzmeier, E. P. Whiteside, D. Lietzke, R. Johnson, 7/27/66.

<u>Horizon</u>	Depth	Description
02 or Al 7-2-1	0-1"	Black (10YR2/1); organic and sand grains mixed; weak medium granular structure; friable; many fine roots; very strongly acid; abrupt smooth boundary.
A2 7-2-2	1-5"	Brown (7.5YR5/2 moist) and pinkish gray (7.5YR6/2 dry); sand; weak fine crumb structure; very friable to loose; many fine roots; very strongly acid; abrupt wavy boundary.
B21ir 7-2-3	5-10"	Reddish brown to dark reddish brown (5YR3/4-4/4); sand; weak medium granular structure; very friable; many fine roots; the upper 1" is transitional between A2 and B21ir; neutral; clear wavy boundary;
B22ir 7-2-4	10-18"	Reddish brown (5YR4/4); sand; weak medium to coarse granular structure; very friable, with occasional cemented nodules; many fine roots; slightly acid; clear wavy boundary.

<u>Horizon</u>	Depth	Description
B3 7-2-5	18-31"	Reddish brown (5YR4/4-5/4); sand; weak thick platy to weak medium subangular blocky structure; very friable; slightly coherent and brittle; slightly acid; abrupt smooth boundary.
C1 7-2-6	31-72"	Reddish brown (5YR5/3-5/4); sand; single grain; loose; slightly acid; abrupt smooth boundary.
	72-120"	Reddish gray (5YR5/2); and reddish brown (5YR4/3); silt and very fine sand; stratified; massive; laminated; very friable; medium acid.

Colors refer to moist conditions, unless otherwise specified.

#### Omega Sand

Baraga County, Michigan. SW1/4, SW1/4, Sec. 8, T49N, R34W. 100 feet west of the Big Lake Location:

landing field.

Jack Pine, Scrub Oak, Reindeer Moss, Blueberries Sweet Fern, Bracken Fern. Vegetation:

Parent Material: Sand.

Slope: 0-1%

Physiography: Outwash Plain.

Drainage: Excessive.

<u>Collectors</u>: D. Franzmeier, E. P. Whiteside, D. Lietzke, R. Johnson. 7/27/66.

Description By: R. Johnson, and E. P. Whiteside.

<u>Horizon</u>	<u>Depth</u>	<u>Description</u>
02 7-3-1a	3/4-0"	Dark reddish brown (5YR2/2) well decomposed leaf litter; weak fine granular structure; many fine fibrous roots; very strongly acid; abrupt smooth boundary.
A3 7-3-1b	0-2"	Very dark gray (5YR3/1) to dark reddish brown (5YR3/2) moist, and pinkish gray (6YR6/2 dry); sand; very weak fine granular structure; very friable; extremely acid; abrupt smooth boundary.
B21 7-3-2	2-8"	Reddish brown (5YR4/4-4/3 moist) and reddish brown (5YR5/4 dry); sand; very weak medium granular structure; very friable; medium acid; clear smooth boundary.
B22 7-3-3	8-17"	Reddish brown (5YR5/4); sand; very weak medium granular structure; very friable; medium acid; clear wavy boundary.

	<u>Horizon</u>	<u>Depth</u>	Description
	B3 7-3-4	17-25"	Strong brown (7.5YR5.6); sand; few reddish brown (5YR5/4) color bands; very weak medium granular structure; very friable; slightly acid; clear wavy boundary.
	C1 7-3-5	25-37"	Light brown (7.5YR6/4); sand; single grain; loose; slightly acid; clear smooth boundary.
	C2 7-3-6* (auger samp)	37-93: le)	Light reddish brown (5YR6/3); sand; single grain; loose; neutral; abrupt smooth boundary.
(nc	C3 ot sampled)	93-99"	Light reddish brown (5YR6/3); sand; with a few 1/8" to 1" thick reddish brown (2.5YR5/4) and reddish gray 5YR5/2) very fine sand and silt strata; The matrix sand is single grain; loose; the strata are massive; very friable; slightly acid; gradual wavy boundary.
(nc	C4 ot sampled)	99-104"	Light reddish brown (5YR6/3); sand; single grain; loose; neutral.

Colors refer to moist conditions unless otherwise stated.

#### Rousseau Fine Sand

Baraga County, Michigan. SW1/2, NW1/4, Sec. 10, Location:

T50N, R34W. 0.2 miles south of the intersection

at Covington Road, then 200 feet west.

Aspen, White Pine, Red Pine, Red Oak, Jack Pine, White Birch, and Hard Maple, with a ground cover Vegetation:

of Bracken Fern, Wintergreen, Blueberries, and

Strawberries.

Parent Material: Sands.

Slope: 11% South.

Physiography: Old Lake Dune.

Drainage: Well Drained.

Collectors: D. Franzmeier, E. P. Whiteside, D. Lietzke,

R. Johnson. 7/29/66.

Description By: E. P. Whiteside, and R. Johnson.

<u>Horizon</u>	Depth	Description
02 7-4-1	1-1/4-0"	Black (10YR2/1) well decomposed leaf litter containing considerable amounts of fine sand; weak fine to medium granular structure; very friable; many fine roots; very strongly acid; abrupt smooth boundary.
A2 7-4-2	0-4"	Brown (7.5YR5/2) moist) and pinkish gray (7.5YR7/2 dry); fine sand; weak medium to coarse granular structure; very friable to loose; few fine roots; very strongly acid; abrupt wavy boundary.
B21ir 7-4-3	4-8"	Reddish brown (5YR4/4); fine sand; weak medium to coarse subangular blocky to weak coarse granular structure; very friable; many fine roots; but less than in the A2 horizon; slightly acid; clear wavy boundary.

<u>Horizon</u>	<u>Depth</u>	Description
B22ir 7-4-4	8-14"	Yellowish red (5YR4/6); fine sand; weak coarse granular to weak fine subangular blocky structure; very friable; few roots; slightly acid; clear wavy boundary.
B3 7-4-5	14-20"	Reddish brown (5YR5/4); fine sand; single grain; loose; with a few weakly cemented nodules 1/4-3/8" in diameter; slightly acid; clear wavy boundary.
C1 7-4-6	20-27"	Reddish brown (5YR5/3); fine sand; single grain; loose; with weakly cemented lenses; slightly acid; abrupt smooth boundary.
C2 7 <del>-</del> 4-7	24-47"	Reddish brown (5YR5/3) fine sand with reddish brown (5YR4/4) color laminae; single grain with weak medium to thick platy laminae; loose to very friable; medium acid; abrupt smooth boundary.
11C3 7-4-8	47-73"	Reddish brown (5YR5/3) very fine sand with 1" to 1/2" thick reddish brown (2.5YR4/4) silt strata; weak thin to medium platy structure; very friable; medium acid; abrupt smooth boundary.
IIIC4 (not sampled	73-78" 1)	Reddish brown (5YR4/3); silt; weak medium subangular block to weak think to medium platy structure; friable; few medium roots; very strongly acid; abrupt smooth boundary.
IVC5 (not sample	78-83'' d)	Reddish brown (5YR5/3); very fine sand; single grain; loose; medium acid; abrupt smooth boundary.

<u>Horizon</u>	<u>Depth</u>	Description
VC6 (not sample	83-87" ed)	Light reddish brown (5YR6/3); fine sand; single grain; loose; slightly acid; abrupt smooth boundary.
VIC7 (not sample	87-121" ed)	Light reddish brown (5YR6/3); sand; single grain; loose; neutral.

Color refers to moist conditions unless otherwise noted.

#### Grayling Sand

Location: Cheyboygan County, Michigan, SW1/4, SE1/4, Sec. 27,

T35N, RZW. 0.23 miles north of Roberts Lake

Road, then 200 feet NE into woods.

Vegetation: Jack Pine, Scrub Oak, Choke Cherry, Bracken

and Sweet Fern.

Parent Material: Sand.

Slope: 0-1%

Physiography: Lake Plain.

<u>Drainage</u>: Excessive.

Collectors: Dr. Franzmeier, S. Alfred, A. Hyde, R. Johnson,

8/1/66.

Description By: S. Alfred, and R. Johnson.

<u>Horizon</u>	<u>Depth</u>	<u>Description</u>
A1 16-1-1	0-1-1/2"	Black (10YR2/1); sand; weak fine granular structure; very friable; slightly acid; abrupt smooth boundary.
A3 16-1-2	1-1/3-3"	Dark yellowish brown (10YR3/4, moist) and grayish brown (10YR5/2, dry) to dark grayish brown (10YR 4/2 dry); sand; very weak coarse granular structure; very friable; strongly acid; clear wavy boundary.
B21 16-1-3	3-7"	Brown to dark brown (7.4YR4/4, moist) to dark yellowish brown (10YR4/4, moist) and light yellowish brown (10YR6/4, dry); sand; very weak coarse granular structure; very friable; medium acid; clear smooth boundary.

<u>Horizon</u>	Depth	Description
B22 16-1-4	7-15"	Yellowish brown (10YR5/6, moist) to dark yellowish brown (10YR4/4, moist) and brownish yellow (10YR6/6, dry); sand; single grain; loose; medium acid; gradual smooth boundary.
B3 16-1-5	15-22"	Yellowish brown (10YR5/4, moist) and yellow (10YR7/6, dry); sand; single grain; loose; medium acid; clear smooth boundary.
C1 16-1-6	22 -44"	Light yellowish brown (10YR6/4) to very pale brown (10YR7/4); sand; single grain; loose; slightly acid; clear smooth boundary.
C2 16-1-7	44-66"	Light yellowish brown (10YR6/4) sand; with a few 1/16" to 1/8" brownish yellow (10YR6/6) color bands; single grain; loose; slightly acid; gradual wavy boundary.
C3 16-1-8 (auger samp	66-122" 1e)	Light yellowish brown (10YR6/4); sand; single grain; loose; slightly acid.

Colors refer to moist conditions unless otherwise noted.

#### Rubicon Sand

Cheboygan County, Michigan. SW1/4, SW1/4, Sec. 5, T35N, R1W. 0.5 miles west off of Highway M-33 on Location:

Hockleburg Road, then 200 feet north.

Red Oak, Aspen, Red Maple, White and Red Pine, Vegetation:

ground cover predominantly of Bracken Fern.

Parent Material: Sand.

Slope: 2% North.

Physiography: High lake plain, bordering moraine.

Drainage: Well drained.

D. Franzmeier, S. Alfred, A. Hyde, R. Johnson. 8/1/66. Collectors:

Description By: S. Alfred and R. Johnson

<u>Horizon</u>	Depth	<u>Description</u>
Al or 02 16-2-1	0-1"	Black (10YR2/1) sand, flecked with light brownish gray (10YR6/2); weak fine granular structure; very friable; very strongly acid; abrupt smooth boundary.
A2 16-2-2	1-6"	Light brownish gray (10YR6/2); sand; very weak medium to coarse granular structure; very friable; very strongly acid; clear wavy boundary.
B21ir 16-2-3	6-10"	Reddish brown (5YR4/4) to dark brown (7.5YR4/4); sand; weak medium to coarse granular structure; very friable; medium acid; clear wavy boundary.

<u>Horizon</u>	<u>Depth</u>	Description
B22ir 16-2-4	10-18"	Dark yellowish brown (10YR4/4); sand; weak coarse granular structure; very friable; medium acid; clear irregular boundary.
B3 16-2-5	18-36"	Light gray (10YR7/2) and yellowish brown (10YR5/6) in equal proportions with a honeycomb pattern; sand; very weak coarse subangular blocky structure to massive in spots; very friable to weakly cemented in chunks; medium acid; clear irregular boundary.
C1 16-2-6	36-60"	Light yellowish brown (10YR6/4); sand; single grain; loose; slightly acid; clear wavy boundary.
C2 16-2-7	60-120"	Light yellowish brown (10YR6/4); sand; single grain; loose; slightly acid.
Ortstein 16-2-8	18-24"	Yellowish brown (10YR5/6) representing 60% of the mass and dark reddish brown (5YR3/4) and pale brown (10YR6/3) representing the major remaining colors; sand; massive; weakly to strongly cemented chunks, chunks are longer than wide and range from 16" to 38" thick and 4" to 6" in diameter, (having the appearance of tree taproots;) medium acid.

Colors refer to moist conditions unless otherwise noted.

## Grayling Sand

Delta County, Michigan. SE1/4, SW1/4, Sec. 34, T41N, R21W. 0.2 miles south of US-2 on -21, Location:

then east 100 feet.

Jack Pine, Reindeer Mosses, Blueberries, and Vegetation:

Sweet Fern.

Parent Material: Sand.

Slope: 3% Northwest.

Physiography: High Lake plain.

Drainage: Excessive.

Collectors: Dr. Franzmeier, and R. Johnson. 7/29/66.

Description By: R. Johnson

<u>Horizon</u>	<u>Depth</u>	Description
A1 21-1-1	0-1"	Black (N2/); sand; weak medium granular structure; very friable; very strongly acid; abrupt smooth boundary.
A3 21-1-2	1-2-1/2"	Brown to dark brown (7.5YR4/2); sand; weak medium granular structure; very friable; very strongly acid; abrupt smooth boundary.
B21 21-1-3	2-1/2-7"	Brown to dark brown (7.5YR4/4); sand; weak coarse granular structure; very friable; strongly acid; clear smooth boundary.
B22 21-1-4	7-12"	Strong brown (7.5YR5/6); sand; very weak coarse granular structure to single grain; medium acid; clear irregular boundary.

<u>Horizon</u>	<u>Depth</u>	Description
B3 21-1-5	12-22"	Light brown (7.5YR6/4) sand with common, coarse, distinct strong brown (7.5YR5/6) color stains in a blotchy pattern which is not due to impeded drainage; single grain; loose; medium acid; gradual smooth boundary.
C1 21-1-6*	22-68"	Light yellowish brown (10YR6/4) to light brown (7.5YR6/4); sand; single grain; loose; medium acid; abrupt smooth boundary.
C2 (not sample	68-101" d)	Light yellowish brown (10YR6/4); sand, with common coarse distinct yellowish brown (10YR5/6) color stains in a blotchy pattern which do not appear to be due to impeded drainage; single grain; loose; strongly acid; abrupt smooth boundary.
C3 (not sample	101-111'' d)	Yellowish brown (10YR5/6); sand; single graind; loose; strongly acid; abrupt smooth boundary.
C4 (not sample	111 <b>-</b> 12 <b>3</b> '' d)	Light yellowish brown (10YR6/4) sand, with three 4" thick yellowish brown (10YR5/8 and 5/4) coarse sand bands; single grain; loose; strongly acid.

# Onaway Fine Sandy Loam

Delta County, Michigan. SW1/4, SW1/4, Sec. 33, T40N, R24W. 2.1 miles north of County Road 410, then 100 feet west off the trail. Location:

Vegetation: Red Maple, White Birch, Balsam Fir, Aspen.

Parent Material: Loam or sandy loam glacial till.

Physiography: Till plain.

<u>Drainage</u>: Well Drained.

Collectors: D. Franzmeier, L. Berndt, R. Johnson. 7/30/66.

Description By: R. Johnson

<u>Horizon</u>	Depth	<u>Description</u>
02 or Al	0-2"	Black (N2/); fine sandy loam with high organic matter content; weak medium granular structure; very friable; many fibrous roots; very strongly acid; abrupt smooth boundary.
A2 21-2-2	2-6"	Reddish brown (5YR5/3), moist) and pinkish gray (5YR7/2 dry); fine sandy loam; weak thick platy structure; friable; few fibrous roots; very strongly acid; abrupt wavy boundary.
B21ir 21-2-3	6-9"	Dark reddish brown (5YR3/4); loam; weak coarse granular structure; friable; many roots; strongly acid; clear wavy boundary.
B22ir 21-2-4	9-12"	Yellowish red (5YR5/6); loam; weak medium subangular blocky structure; very friable; few roots; strongly acid; clear irregular boundary.

<u>Horizon</u>	<u>Depth</u>	Description
A'2× 21-2-5	12-18"	Reddish brown (5YR5/3 moist) and pinkish gray (7.5YR7/2 dry); loam; reddish brown (5YR4/4) on the interior of some peds; the lower part of the horizon tongues into the B;2lt; weak coarse subangular blocky structure to massive; vesicular; very hard and brittle when dry; medium acid, clear irregular boundary.
B'21t 21-2-6	18-24"	Yellowish red (5YR5/6) on the exterior of peds and reddish brown (5YR4/4) interior of peds; loam; many clay skins on ped faces and in root channels; weak medium to coarse subangular blocky structure; firm; few coarse roots; slightly acid; clear wavy boundary.
B'22t 21-2-7	24-28"	Reddish brown (5YR4/3); loam; with reddish brown (5YR5/4) coatings on the exterior of peds and heavy reddish brown (5YR5/3) clay flows along root channels and on ped faces; moderate medium subangular blocky structure; firm; few coarse roots; neutral with some limey pebbles; clear smooth boundary.
C1 21-2-8*	28-42"	Light brown (7.5YR6/4) to brown (7.5YR5/4); loam-fine sandy loam; weak medium subangular blocky structure; friable; calcareous.

Colors refer to moist conditions unless otherwise stated. Textural development and development of the spodic upper sequum is modal for the series.

## Onaway Fine Sandy Loam

Location:

Delta County, Michigan. NW1/2, SE1/4, Sec. 7, T37N, R24W. 2.3 miles south of County Road 535 on B-35 then 0.4 miles southwest on the logging

trail, then 50 feet south.

Vegetation: Hard Maple, Beech.

Parent Material: Loam glacial till.

Slope: 2% North.

Physiography: Top of low lying drumlin.

Drainage: Well drained.

Collectors: D. Franzmeier, R. Johnson, L. Berndt.

Description By: R. Johnson

<u>Horizon</u>	<u>Depth</u>	Description
02 21-3-1	1-0"	Black (10YR2/1) well decomposed leaf litter; moderate medium granular structure; very friable; many fibrous roots; mildly alkaline; abrupt smooth boundary.
A2 21-3-2	0-3-1/2"	Brown (7.5YR5/2 moist) and light gray to gray (5YR6/1 dry); fine sandy loam; weak medium granular structure; very friable; few fibrous roots; slightly acid; abrupt wavy boundary.
B21ir 21-3-3	3-1/2-6"	Dark reddish brown (5YR3/4); fine sandy loam; weak coarse subangular blocky structure; friable; many fine roots; neutral; clear wavy boundary.
B22ir 21-3-4	6-9"	Reddish brown (5YR4/4); fine sandy loam; weak coarse granular structure; friable; many fine roots; mildly alkaline; abrupt wavy boundary.

<u>Horizon</u>	Depth	Description
A'2x and B'21tx 21-3-5	9-13"	Light reddish brown (5YR6/3, moist) and pinkish gray (5YR7/2 dry) fine sandy loam, representing the A'2 portion and dark reddish brown (5YR3/4) loam representing the B'2ltx portion; the A'2 consists of heavy coatings up to l" thick around the peds of finer textured material; massive breaking to weak coarse subangular blocky structure; vesicular; very hard and brittle when dry; no roots; mildly alkaline; clear irregular boundary.
B'22t 21-3-6	13-21"	Dark reddish brown (5YR3/4) to reddish brown (5YR4/4); coarse clay loam; heavy clay flows in the root channels and on ped faces; moderate coarse prismatic breaking to weak medium subangular blocky structure; very firm; few coarse roots; mildly alkaline; clear smooth boundary.
C1 21-3-7*	21-40"	Light brown (7.5YR6/4) to brown (7.5YR5/4); silt loam; moderate thick platy structure breaking to weak fine subangular blocky structure; friable; few coarse roots; calcareous.

This profile represents the stronger side of the series for textural development. The upper spodic sequum is modal for the series.

### Kalkaska Sand

Location: Emmet County, Michigan, SE1/4, SE1/4, NE1/4,

Sec. 36, T35N, R4W. 200 feet west of the road.

<u>Vegetation</u>: Hard Maple, Black Cherry.

Parent Material: Sand.

Slope: 1% West.

Physiography: High lake plain.

Drainage: Well Drained.

Collectors: D. Franzmeier, R. Johnson, S. Alfred, A. Hyde.

8/2/66.

Description By: S. Alfred, and R. Johnson.

<u>Horizon</u>	<u>Depth</u>	Description
02 24-1-1	2-0"	Black (10YR2/1) well decomposed leaf litter with a high proportion of mineral soil; weak medium granular structure; very friable; many fine roots; very strongly acid; abrupt smooth boundary.
A 2 24-1-2	0-9"	Light brownish gray (10YR6/2); sand; single grain; loose; few fine roots; very strongly acid; abrupt irregular boundary.
B21h 24-1-3	9-11"	Dark reddish brown (5YR2/2); sand; weak medium granular structure; massive in chunks; very friable with some strongly cemented chunks of ortstein occurring in the lower part of this horizon and in the B22ir, B23ir, and the upper B3 horizon; many fine roots penetrate the ortstein chunks; very strongly acid; abrupt irregular boundary.

<u>Horizon</u>	Depth	Description
B22hir 24-1-4	11-15"	Dark brown (7.5YR3/2); sand; very weak coarse granular to medium subangular blocky structure; massive in chunks; very friable with strongly cemented chunks of ortstein; very strongly acid; clear irregular boundary.
B23ir 24-1-5	15-23"	Brown to dark brown (7.5YR4/4); sand; very weak coarse to medium granular structure; very friable with a few weakly cemented chunks of ortstein; medium acid; clear irregular boundary.
B3 24-1-6	23-38"	Yellowish brown (10YR5/4); sand; very weak coarse granular structure; very friable; medium acid; gradual wavy boundary.
C1 24-1-7	38-75"	Light yellowish brown (10YR6/4); sandy-loamy sand; single grain; loose; slightly compacted just above the IIC2 horizon; medium acid; abrupt smooth boundary.
11C2 24-1-8	75-90"	Light yellowish brown (10YR6/4) sand; with dark brown (10YR4/3) to dark yellowish brown (10YR4/4) loamy sand bands; single grain matrix with massive vesicular bands; loose with slightly hard and slightly brittle bands; medium acid; abrupt wavy boundary.
111C3 24-1-9	90-128"	Light yellowish brown (10YR6/4) sand, with a few dark yellowish brown (10YR4/4) color bands in the upper 10 inches of the horizon; single grain; loose; slightly acid.

<u>Horizon</u>	<u>Depth</u>	Description
Ortstein (sampled s 24-1-10*	eparately)	The ortstein occurs in columnar chunks extending from the lower part of the B2lh horizon into the upper part of the B3 horizon.  Approximately 30% of the surface area of the pit occupied by the B2lh, B22ir, B23ir, and B3 consists of ortstein material. Colors are predominantly dark reddish brown (5YR2/2) and dark brown (7.5YR3/2) with some brown (7.5YR5/3) and dark yellowish brown (10YR4/4); sand; massive; strongly cemented; roots extend 60" deep in tongues of "B"; very strongly acid; abrupt irregular boundary.

#### Hiawatha Sand

Location: Houghton County, Michigan. NW1/4, SE1/4, Sec. 7,

T53N, R35W. 0.5 miles west of Toivola, then 0.2 miles south and 0.2 miles west on the logging

road, then 100 feet south.

<u>Vegetation</u>: Cut over Hard Maple, Quack Grass, Timothy sod.

Parent Material: Sand.

Slope: 1% Complex.

Physiography: Outwash Plain.

Drainage: Well drained.

Collectors: D. Franzmeier, E. P. Whiteside, D. Lietzke,

R. Turner, R. Johnson. 7/27/66.

<u>Description By</u>: R. Johnson and E. P. Whiteside.

<u>Horizon</u>	<u>Depth</u>	Description
A1 31-1-1	0-2"	Black (5YR2/1); loamy sand; weak granular structure; very friable; medium acid; abrupt smooth boundary.
A2 31-1-2	2-8"	Gray (5YR5/1) to dark gray (5YR4/1) and light gray (5YR6/1 dry); loamy sand; weak medium to coarse granular structure; very friable; occasional tongues of A2 extending into the B2lhir; medium acid; abrupt wavy boundary.
B21hir 31-1-3	8-11"	Dark reddish brown (5YR2/2); loamy sand; weak medium to coarse granular to weak fine subangular blocky structure; very friable; very strongly acid; abrupt wavy boundary.

<u>Horizon</u>	<u>Depth</u>	<u>Description</u>
B22ir 31-1-4	11-17"	Dark reddish brown (5YR3/4); loamy sand; weak coarse granular to weak medium subangular blocky structure; very friable; few cemented tongues of ortstein which extend to depths of 27"; medium acid; clear wavy boundary.
B31 31-1-5	17-25"	Reddish brown (5YR4/4) to yellowish red (5YR4/6); sand; weak medium to coarse granular structure; very friable; medium acid; clear wavy boundary.
B32 31-1-6	25-33"	Reddish brown (5YR5/4); sand; weak medium to coarse granular structure; very friable; medium acid; clear wavy boundary.
C1 31-1-7	33-60"	Brown (7.5YR5/4); sand; weak fine subangular blocky structure to single grain; very friable to loose; slightly acid; abrupt smooth boundary.
C2 31-1/8	60-90"	Brown (7.5YR5/4) sand, with a few thin reddish brown (5YR5/3) fine sand lenses; single grain; loose; slightly acid; abrupt smooth boundary.
C3 31-1-9* (sampled wi	90-110" th auger)	Brown (7.5YR5/4); sand; single grain; loose; slightly acid.

# Munising Fine Sandy Loam

Houghton County, Michigan. SW1/4, SW1/4, Sec. 25, T54N, R34W. 150 feet north of the road. Location:

Vegetation: Hard Maple.

Parent Material: Sandy loam glacial till.

Slope: 3% West.

Physiography: Moraine.

Drainage: Well drained.

D. Franzmeier, E. P. Whiteside, D. Lietzke, R. Johnson. 7/27/66. Collectors:

Description By: R. Johnson and E. P. Whiteside.

<u>Horizon</u>	<u>Depth</u>	<u>Description</u>
02 31-2-1	1-0"	Black (5YR2/1) well decomposed leaf litter; weak fine granular structure; friable; very strongly acid; abrupt wavy boundary.
A2 31-2-2	0-5"	Gray (5YR5/1) to dark gray (5YR4/1); fine sandy loam; weak fine subangular blocky structure; friable; strongly acid; abrupt wavy boundary.
B21hir 31-2-3	5 <b>-</b> 9"	Very dusky red (2.5YR2/2) representing the primary color and dark reddish brown (5YR3/3); fine sandy loam; weak coarse granular to weak medium subangular blocky structure; friable with a few weakly cemented chunks; very strongly acid; clear wavy boundary.

<u>Horizon</u>	Depth	Description
B22ir 31-2-4	9-17"	Dark reddish brown (5YR3/4) to reddish brown (5YR4/4); loamy fine sand; weak coarse subangular blocky, breaking to weak coarse grandular structure; friable; medium acid; clear wavy boundary.
B3 31-2-5	17-22"	Reddish brown (5YR4/3); loamy fine sand; weak coarse subangular blocky, breaking to weak medium grandular structure; friable; medium acid; clear wavy boundary.
A'21 31-2-6	22-27"	Reddish brown (5YR5/4); loamy fine sand; weak fine subangular blocky structure; slightly hard when dry; medium acid; clear smooth boundary.
A'22× 31-2-7	27-40"	Reddish brown (5YR5/3); loamy fine sand; reddish brown (2.5YR4/4) remnants of Bt horizon with thin clay flows in root channels and in pores; weak thick platy breaking to weak medium platy structure; vesicular; hard and brittle when dry strongly acid; gradual wavy boundary.
A'23 and B'21t 31-2-8	40-48"	Reddish brown (5YR5/3) representing A'23 and reddish brown (2.5YR4/4) representing the B'2lt; loamy fine sand; weak thick platy structure; friable when moist and slightly brittle when dry; strongly acid; gradual wavy boundary.
B'22t and A'24 31-2-9	48-66"	Reddish brown (2.5YR4/4) loamy fine sand, with heavy coatings of light reddish (5YR6/3) and reddish gray (5YR5/2) loamy fine sand; few thin clay flows in pores and vesicular where present; weak thick platy structure; friable; strongly acid; gradual wavy boundary.

<u>Horizon</u>	<u>Depth</u>	Description
B'23t 31-2-10	66-79"	Reddish brown (2.5YR4/4); sandy loam; many clay flows along root channels, in pores, and on ped faces; weak coarse subangular blocky structure; friable; medium acid; abrupt smooth boundary.
11C1 31-2-11	79 <b>-</b> 95"	Reddish brown (2.5YR4/4) sandy loam, with few reddish brown (5YR5/3) sand lenses; massive in the matrix with single grain sand lenses; friable matrix with loose sand lenses; medium acid; abrupt smooth boundary.
111C2 31-2-12	95-115"	Reddish brown (2.5YR4/4) sandy loam with dark reddish brown (2.5YR3/4) silty clay loam lenses; massive; friable to firm; medium acid; abrupt smooth boundary.
IVC3 31-2-13*	115-122"	Reddish brown (2.5YR4/4); sandy loam; massive; friable; slightly acid.

Colors refer to moist conditions. Roots are concentrated in the 02, B21hir, and B22ir horizons with some concentrated above the fragipan. A few fine roots extend into the B'22t and A'24 horizon. An estimate of the cobbles and stones over 3 inches in the profile is approximately 2%.

#### Hiawatha Sand

Location:

Houghton County, Michigan. NW1/4, NW1/4, Sec. 2. T54N, R34W. 1.3 miles south of the Houghton-Hancock bridge on M-26, then west 200 feet.

Vegetation: Red Oak, Hard Maple, Ironwood.

Parent Material: Sands.

Slope: 12% East.

Physiography: Moraine.

Drainage: Well drained.

<u>Collectors</u>: D. Franzmeier, E. P. Whiteside, D. Lietzke, R. Johnson. 7/28/66.

Description By: R. Johnson

<u>Horizon</u>	<u>Depth</u>	<u>Description</u>
A1 31-3-1	0-1-1/2	Black (5YR2/1); loamy sand; weak fine granular structure; very friable; many fine fibrous roots; very strongly acid; abrupt smooth boundary.
A2 31-3-2	1-1/2-7"	Gray (5YR5/1 moist) and light gray to gray (5YR6/1 dry); sand; weak coarse granular to weak fine subangular blocky structure; very friable; few fine roots; very strongly acid; abrupt irregular boundary.
B21h 31-3-3	7-11"	Dark reddish brown (5YR2/2) representing 90% of the horizon and dark reddish brown (5YR3/3) representing the rest; sand; weak coarse subangular blocky structure to massive; very friable with strongly cemented chunks which represent approximately 20% of the surface area of the pit sampled and occurring in the lower B2lh, and the B22ir; many fine roots in the friable portion, very strongly acid; abrupt irregular boundary.

<u>Horizon</u>	<u>Depth</u>	Description
B22ir 31-3-4	11-23"	Dark reddish brown (5YR3/4); sand; weak coarse granular to weak fine subangular blocky structure; very friable with some strongly cemented chunks; many fine roots; very strongly acid; clear irregular boundary.
B3 31-3-5	23-24"	Reddish brown (5YR5/4 to 2.5YR5/4); sand; single grain; loose with massive brittle chunks; medium acid; clear wavy boundary.
C1 31-3-5	34-66"	Reddish brown (5YR5/4) to brown (7.5YR5/4); sand, with a few 1/8" to 1/4" dark reddish brown (5YR3/4) color bands occurring between a depth of 60 and 66 inches; single grain; loose; medium acid; clear smooth boundary.
C2 31-3-7	66-123"	Brown (7.5YR5/4) to light brown (7.5YR6/4); sand; single grain; loose; slightly acid.
Ortstein 31-3-8* (sampled se	parately)	The ortstein represents approximately 20% of the surface area of the pit in an area occurring in the lower part of the B2lh, and B22ir horizons. Colors of the ortstein are the same as those represented in the B2lh and B22ir horizons in about equal proportions. The chunks are strongly cemented. No roots penetrate the ortstein. The pH is very strongly acid.

# McBride Loamy-Fine Sand

Lake County, Michigan. NW1/4, SE1/4, Sec. 23, T20N, R11W. 3/8 miles north of Kellogg Tower Road, then 100 feet west into the woods. Location:

<u>Vegetation:</u> Hard maple:

Parent Material: Sandy loam glacial till.

<u>Slope</u>: 3-6% complex. Southwest aspect.

Physiography: Morainic.

Drainage: Well drained.

Collectors: D. Franzmeier, R. Johnson. 8/3/66.

Description By: R. Johnson

<u>Horizon</u>	<u>Depth</u>	<u>Description</u>
A 1 43 - 1 - 1	0-4"	Very dark gray (10YR3/1); loamy fine sand; moderate medium granular structure; friable; very strongly acid; abrupt smooth boundary.
A2 43-1-2	4-6"	Dark gray (10YR4/1) to dark grayish brown (10YR4/2); loamy sand; weak medium subangular blocky structure; very friable; traces of original A2 horizon are discernable, however most has been mixed, possibly by earthworms or wind throw; very strongly acid; clear wavy boundary.
B2ir 43-1-3	6 - 1 4"	Dark reddish brown (5YR3/4); loamy fine sand; weak medium subangular blocky structure; very friable; very strongly acid; clear wavy boundary.

<u>Horizon</u>	<u>Depth</u>	Description
A ' 2 1 43 - 1 - 4	14-20"	Brown (7.5YR5/2); loamy sand; weak medium subangular blocky structure; very friable; strongly acid; clear wavy boundary.
A'22× 43-1-5*	20-34"	Reddish gray (5YR5/2) and pinkish gray (5YR7/2); loamy sand; massive; vesicular; very hard when dry; brittle; very strongly acid; gradual irregular boundary.
B'2lt and Al23x (not sample		Reddish brown (5YR4/3) sandy clay loam, with thick reddish gray (5YR5/2) coatings around peds and as tongues; thin clay flows on some ped faces and in pores; weak thick platy structure; vesicular; very hard and brittle when dry; very strongly acid; gradual wavy boundary.
B'22t (not sample	43-50'' d)	Dark reddish brown (5YR3/4) to reddish brown (5YR4/4); sandy clay loam; many thin clay coatings on ped faces and in root channels; weak medium subangular blocky structure; firm; medium acid; clear wavy boundary.
Cl (not sample	50-78" d)	Brown (10YR5/3) to yellowish brown (10YR5/4); sandy loam; massive; friable; clacareous.

This profile is the same site as the McBride in the Nicolaos John Yassoglou PhD Thesis.

# Oakville Loamy Fine Sand

Macomb County, Michigan. NE1/4, SW1/4, Sec. 9, Location:

T3N, R12E. 500 feet east of the intersection of Odieon and Woodmire Streets, then 100 feet south.

Black Cherry, Ash, Maple, White and Blavk Oak, Vegetation:

and Tulip Poplar.

Parent Material: Sand and Fine sand.

<u>Slope</u>: 1%.

Physiography: Level beach ridge.

Drainage: Well drained. Water table at 89".

<u>Collectors</u>: D. Franzmeier, E. P. Whiteside, B. Watson, R. Johnson. 8/4/66.

Description By: B. Watson.

<u>Horizon</u>	<u>Depth</u>	Description
02 50-1-1	1-0"	Black (10YR2/1) well decomposed leaf litter; weak fine granular structure; very friable; many fine fibrous roots; slightly acid; abrupt smooth boundary.
A2 50-1-2	0-2"	Dark grayish brown (10YR4/2); loamy fine sand; weak coarse granular structure; very friable; many fibrous roots; strongly acid; abrupt wavy boundary.
B21 50-1-3	2-6"	Brown to dark brown (7.4YR4/4) to strong brown (7.5YR5/6); loamy fine sand; weak coarse granular structure; very friable; many roots; medium acid; clear wavy boundary.
B22 50-1-4	6-12"	Strong brown (7.5YR5/6); fine sand- loamy fine sand; weak medium to coarse granular structure; very friable; strongly acid; clear wavy boundary.

<u>Horizon</u>	<u>Depth</u>	Description
B23 50-1-5	12-20"	Yellowish brown (10YR5/6); fine sand; weak medium granular structure; very friable; few roots; very strongly acid; clear smooth boundary.
B3 50-1-6	20-29"	Yellowish brown (10YR5/4-5/6); fine sand; single grain; loose; very few roots; medium acid; abrupt wavy boundary.
11C1 50-1-7	29-47"	Yellowish brown (10YR5/4); sand; containing 5-10% fine gravel; single grain; loose; many coarse roots; slightly acid; abrupt wavy boundary.
111C2 50-1-8	47-66"	Light yellowish brown (10YR6/4) fine sand with common fine distinct strong brown (7.5YR5/6) mottles; single grain; loose when moist, non-sticky when wet; medium acid; gradual wavy boundary.
111C3 50-1-9*	66-122"	Light yellowish brown (10YR6/4); fine sand; single grain; loose when moist; non-sticky when wet; calcareous.

### Omega Fine Sand

Location: Marquette County, Michigan. SW1/4, SE1/4, Sec. 27,

T46N, R25W. 24 paces east and 131 paces north of the road center at the intersection just east of

the railroad crossing.

Vegetation: Jack Pine, Sweet Fern, Reindeer Mosses, and

Blueberries.

Parent Material: Sand.

<u>Slope</u>: 0-1%.

Physiography: Outwash plain.

Drainage: Excessive.

Collectors: D. Franzmeier, E. P. Whiteside, D. Lietzke,

R. Johnson.

<u>Description By</u>: R. Johnson, and E. P. Whiteside.

<u>Horizon</u>	<u>Depth</u>	Description
Al 52-1-1 (Al and A2 together)	0-1" sampled	Black (5YR2/1); fine sand; weak medium granular structure; very friable; very strongly acid; abrupt smooth boundary.
A2 52-1-1	1-3"	Brown (7.5YR5/2); fine sand; weak fine granular structure; very friable; extremely acid; abrupt wavy boundary.
B21 52-1-2	3-8"	Brown to dark brown (7.5YR4/2-4/4 moist) and brown (7.5YR5/4 dry); fine sand; weak medium granular structure; very friable; medium acid; clear smooth boundary.

<u>Horizon</u>	<u>Depth</u>	<u>Description</u>
B22 52-1-3	8-12"	Brown to dark brown (7.5YR4/4 moist) and light brown (7.5YR6/4 dry); fine sand; weak medium granular structure; very friable; slightly acid; clear smooth boundary.
B3 52-1-4	12-18"	Brown to dark brown (7.5YR4/4 moist) and light brown (7.5YR6/4 dry); fine sand; weak medium to coarse granular structure; very friable; slightly acid; clear smooth boundary.
C1 52-1-5	18-28"	Reddish brown (5YR5/3 moist) and light brown (7.5YR6/4 dry); fine sand; single grain; loose, slightly acid; abrupt smooth boundary.
C2 52-1-6	28-37"	Reddish brown (5YR5/3 moist) and light brown (7.5YR6/4 dry); sand; single grain; loose; neutral; abrupt smooth boundary.
C3 52-1-7	37-43"	Light reddish brown (5YR6/3-6/3) fine sand with a thin reddish brown (5YR4/4) color band, 1/32" thick; weak thick platy structure to single grain; very friable to loose; neutral; abrupt smooth boundary.
C4 52-1-8*	43-94"	Light reddish brown (5YR6/3); sand; single grain; loose; neutral.

# McBride Sandy Loam

Osceola County, Michigan, SE1/4, SE1/4, Sec. 36, T19N, R10W. 225 feet north of the road.

Vegetation: Aspen, Hard Maple, Cherry, Ash.

Parent Material: Sandy loam to sandy clay loam glacial till.

Slope: 3-4% complex. East aspect.

Physiography: Moraine.

Drainage: Well drained.

Collectors: Dr. Franzmeier, H. Weber, R. Johnson. 8/3/66.

Description By: H. Weber and R. Johnson.

Horizon	<u>Depth</u>	<u>Description</u>
Â1 67-1-1	0-2"	Very dark gray (10YR3/1); sandy loam; weak medium granular structure; very friable; neutral; abrupt smooth boundary.
A 2 6 7 <b>-</b> 1 - 2	2-8"	Reddish brown (5YR5/3); light sandy loam; weak medium sub-angular blocky structure; very friable; very strongly acid; clear wavy boundary.
B2ir 67-1-3	8-13"	Dark reddish brown (5YR3/2); sandy loam; weak medium subangular blocky structure; friable; very strongly acid; clear wavy boundary.
A ' 2× 67-1-4	13-29"	Grayish brown (10YR5/2) representing 70% of the color, and dark yellowish brown (10YR4/4) representing the rest of the color; loamy sand; massive; vesicular; very hard and brittle when dry; medium acid; gradual irregular boundary.

<u>Horizon</u>	<u>Depth</u>	Description
A'2x and B'21t 67-1-5	29-43"	Light reddish brown (5YR6/3); loamy sand representing the A'2 portion and dark reddish brown (5YR3/4) sandy clay loam representing the Bt portion; thick clay flows in old root channels and pores; weak coarse subangular blocky structure; vesicular; very firm; brittle; strongly acid; gradual irregular boundary.
B'22t 67-1-6	43-73"	Reddish brown (5YR4/3); sandy clay loam; thick clay flows on ped faces and in root channels; weak coarse subangular blocky stucture; firm; neutral; clear wavy boundary.
C1 67-1-7*	73-111"	Reddish brown (5YR4/3); heavy sandy loam; massive; friable; calcareous.

#### Kalkaska Sand

Location: Osceola County, Michigan. SE1/4, SE1/4, NE1/4, Sec. 10, R10W, T20N. 200 feet west of the road.

<u>Vegetation</u>: Red Maple, Aspen, Bracken Fern.

Parent Material: Sand.

<u>Slope</u>: 3-4% east.

Physiography: Moraine.

Drainage: Well Drained.

Collectors: Dr. Franzmeier, H. Weber, R. Johnson. 8/4/66.

Description By: H. Weber and R. Johnson

ŀ	<u>Horizon</u>	<u>Depth</u>	Description
(	A+ 67-2-1 (A+ and 02 : together)	3-1" sampled	Very dark gray(10YR3/1) when crushed, sand, appears as a mixture of black (N/2) and light gray (10YR6/1) imparting a salt and pepper effect; single grain; loose; very strongly acid; abrupt smooth boundary.
	02 67-2-1	1-0"	Black (N/2) well decomposed leaf litter; moderate medium granular structure; very friable; many fibrous roots; very strongly acid; clear smooth boundary.
	A21 67-2-2	0-4"	Grayish brown (10YR5/2); sand; very weak medium granular structure; very friable; few fibrous roots; medium acid; abrupt irregular boundary.
	A22 67-2-3	4-13"	Light gray to gray (10YR6/1 moist) and light gray (10YR7/1 dry); sand; very weak coarse to medium granular structure; very friable; medium acid; abrupt irregular boundary.

<u>Horizon</u>	<u>Depth</u>	Description
B21h 67-2-4	13-15"	Dark reddish brown (5YR2/2-3/2); sand; weak coarse to medium subangular blocky structure to massive in places; very friable; weakly cemented in places; many fibrous roots, but no roots in cemented chunks; very strongly acid; abrupt irregular boundary.
B22ir 67-2-5	15-19"	Dark reddish brown (5YR3/3-3/4) sand with patches of reddish brown (5YR4/4); weak coarse subangular blocky structure to massive in spots; very friable to strongly cemented in spots; few roots; very strongly acid; clear irregular boundary.
B23ir 67-2-6	19-27"	Dark yellowish brown (10YR4/4) to brown or dark brown (7.5YR4/4) representing 90% of the color, and dark brown (10YR3/3) representing the rest; sand; weak coarse subangular blocky structure to massive in spots; very friable to strongly cemented chunks; strongly acid; clear irregular boundary.
B3 67-2-7	27-37"	Yellowish brown (10YR5/4) sand with a few dark yellowish brown (10YR4/4) concretions; weak coarse granular structure; very friable; medium acid; clear wavy boundary.
C1 67-2-8	37-63"	Light yellowish brown (10YR6/4) to pale brown (10YR7/4); sand; single grain; loose; slightly acid; gradual wavy boundary.

<u>Horizon</u>	<u>Depth</u>	Description
C2 67-2-9	63-86"	Light yellowish brown (10YR6/4) sand with a few 1/4" thick yellowish brown (10YR5/6) color bands of light loamy sand in the lower ten inches of the horizon; single grain; loose; the bands are coherent and very friable; medium acid; gradual wavy boundary.
C3 67-2-10	86-119"	Light yellowish brown (10YR6/4); sand; single grain; loose; medium acid.
Ortstein 67-2-11* (sampled se	parately)	Occurs in the lower part of the B21h, the B22ir, and the B23ir horizons in the form of chunks. The ortstein represent approximately 10% of the surface area of the pit occupied by these horizons. The colors of the cemented chunks includes those of the B21h, B22ir, and the B23ir horizons, in about equal proportions. The chunks are strongly cemented.

## Eastport Sand

Location: St. Clair County, Michigan. SW1/4, SW1/4, SE1/4, NE1/4, Sec. 9, T7N, R17E.

<u>Vegetation</u>: Aspen and Choke Cherry, with ground cover of

weeds and grasses.

Parent Material: Sand.

Slope: 5% West. Description written near the slope crest.

Physiography: First beach ridge off of Lake Huron.

Drainage: Well drained. Water table at 119".

D. Franzmeier, E. P. Whiteside, G. Landtiser, J. Larson, and K. Mettert. 8/4/66.

Description By: E. P. Whiteside

<u>Horizon</u>	<u>Depth</u>	Description
Ap 74-1-1	0-7"	Very dark gray (10YR3/1); sand; weak fine granular structure; very friable; strongly acid; abrupt smooth boundary.
A2 74-1-2	7-10"	Brown (10YR5/3); sand; very weak fine crumb structure to single grain; very friable to loose; slightly acid; abrupt wavy boundary.
B1 74-1-3	10-13"	Light yellowish brown (10YR6/4) to brown (7.5YR5/4); sand; very weak coarse granular structure to single grain; very friable to loose; slightly acid; clear wavy boundary.
B21 74-1-4	13-19"	Brown (7.5YR5/4) to strong brown (7.5YR5/6); sand; weak coarse granular to weak medium subangular block structure; very friable, with some weakly cemented chunks 1/2 to 1" in diameter; neutral; gradual wavy boundary.

<u>Horizon</u>	<u>Depth</u>	Description
B22 74-1-5	19-26"	Brown (7.5YR5/4) to strong brown (7.5YR5/6); sand; weak coarse granular to weak medium subangular block structure; very friable with some weakly cemented chunks 1/2-1" in diameter; slightly acid; clear wavy boundary.
B3 74-1-6	26-34"	Yellowish brown (10YR5/4); sand; weak coarse granular structure to single grain; very friable to loose; slightly acid; clear wavy boundary.
C1 74-1-7	34-52"	Brown (10YR5/3); sand; single grain; loose; slightly acid; abrupt smooth boundary.
C2 74-1-8*	52-85"	Grayish brown (2.5Y5/2-10YR5/2); sand, with some darker colored coarse sand strata; single grain; loose; slightly acid; abrupt smooth boundary.
C3 (not sample	85-98'' d)	Grayish brown (2.4Y5/2); coarse sand, and fine gravel; single grain; loose; calcareous; abrupt smooth boundary.
C4 (not sample	98-119" d)	Grayish brown (2.5Y5/2) sand and fine gravel with dark brown (7.5YR4/4) staining; single grain; loose; calcareous; abrupt smooth boundary.
C5 (not sample	119-125" d)	Gray (10YR5/1); sand; single grain; nonsticky when wet; calcareous.

APPENDIX III

Laboratory Data

Table 12. Laboratory data for profiles studied

		4	0xalat	ate	tr	ate-	Pyro.	1 -	-	٥	P. D. *	
		ueptn inches	₽ %	۸ <u>۱</u> %	-≫ o)		e % -		ر د د % د	`.   ×	ς χχ.	C]av
(Vilas) Rubicon												ŀ
	A1	-	0	.03	. 12	.03	:	!	9	2.88	;	4.9
2-1-2	A2 B21:5	1-1/2-4	.04 26	0.	0	-0-	1 6		.75	74.		2.2
2-1-2 2-1-4	<b>4</b> C	, ו	7 -		-		• • • • • • • • • • • • • • • • • • •	٥	<u>م</u> د	.00	ر. مر	··
	1 K	- ?	- C		<b>-</b> C		- ! • !	07.	· ·			
2-1-6	B32	21-27	$\circ$	<u></u>	$\circ$					90		- o
<del>-</del>	۰-	7-	0	.05	0	03				70		١٧
2-1-8	C2	-6	0	0.0	0	03				- ) •		
+	C3	<u> </u>	0	0.	0	0.						9
-1-10 Avg.	1		_	. 15	_	0.	Ξ.	. 26	5	61.	.25	6
-1-10 Light Ort.	Chunks		60.	.25	71.	.05	!	:	.62	1		<u> </u>
-1-10 Dark Ort.	Chunks		. 20	.33		. 12			σ			
Munising												
7-1-1	٦	0-1	0	.03	7	.02			6.83	09.9		ص ص
7-1-2	A2	ģ	0	<u></u>	2	.02	;		ż			m
7-1-3	2	_	2	19:	$\infty$	.42	<b>79</b>	1.07	ن	.5	2.20	•
7-1-4	B22ir	-2	. 23	.43		. 15	.41	9	0	٠.	$\dot{\omega}$	•
7-1-5	3	-2	0	<u>e</u>	7	80.			m	2		
7-1-6	12	7-	0	<u>.</u>	7	80.	. 24	.02		_	.03	•
7-1-7	121	7-	_	.07	4	[	04.	80.		0		
7-1-8	-2	9	.03	[	$\boldsymbol{\omega}$	[0.				0		•
7-1-9	<u>.</u>	62-82	.03	<u>.</u>	.35	[0						10.1
7-1-10	C2	7	<u>.</u>	<u>.</u>		-						•

Table 12, Continued

inches % % % % % % % % % % % % % % % % % % %	3	1 (	0xa1	ate	1 +	ate-	Pyro.	+		۵	P. D. 4	
2-A1 0-1 .04 .01 .44 .05 8.58 6.00 7.5 16 1.5 17 .01 .01 .01 .01 .01 .01 .01 .01 .01 .01	. 100	inches	Fe.	% A1.	-   0		e %-	、 ⋖	ς ς γ			% <b>-</b>
2   1-5   1-	2-	Ī-0	70.	0	77.	.05			8.58	0		•
2   10-18   14   38   23   14   17   182   13   124   15   15   15   15   15   15   15   1	2 0	-5	.01 25	07	- 20 20	.0.	~	C	4 6	-7	~	•
3 18-31 .02 .06 .05 .02 .05 .51 .04 .03  1 31-72 .01 .06 .05 .02 tr .44 tr .11  2 3/4-0 .05 .20 .33 .05 tr  2 3/4-0 .07 .05 .18 .04 3.98 4.32  2 12-8 .16 .34 .27 .07 .24 .52 .44 .32  2 17-25 .07 .11 .10 .07  3 17-25 .07 .11 .10 .07  2 17-25 .07 .11 .10 .07  2 1-1/2-0 .03 .05 .14 .01  2 1-1/2-0 .03 .05 .14 .01  2 1-1/2-0 .03 .05 .14 .01  3 14-20 .05 .09 .03  2 27-47 .02 .04 .08 .03  2 27-47 .02 .04 .08 .03  2 27-47 .02 .04 .08 .03  3 18-72  2 27-47 .02 .04 .08 .03  3 18-72  3 18-72  3 18  3 19 4.32  4 10  5 10  5 10  6  6  7 10	10	<u>-</u> 0	71.	m		71	<b>`</b> —	$\infty$	- m	7	<b>`</b> —	• •
2 3/4-0 .07 .05 .18 .04 3.98 4.32 -2 2 .03 .05 .10 .11 .13 .22 .10 .11 .13 .22 .22 .22 .23 .14 .27 .07 .24 .52 .44 .32 .22 .22 .23 .17 .25 .07 .11 .10 .07 .11 .13 .41 .22 .10 .10 .10 .10 .10 .10 .10 .10 .10 .10		8-3	.02	0	.05	.02	0	5		0	0 7	
2 3/4-0 .07 .05 .18 .04 3.98 4.32	<u> </u>	2-12	.05	20	33.	.05	_	†			5	 
2 3/4-0 .07 .05 .18 .04 3.98 4.32 -2.0												
2 0-2 0.9 06 .22 03 1.17 1.13 2.2 2. 2. 2. 3. 44 .32 .22 2. 2. 8-17 09 .19 .15 .11 .13 .41 .22 .10 .10 1. 1. 13 .41 .22 .10 .10 1. 1. 13 .41 .22 .10 .10 1. 1. 15 .25 .37 .02 .03 .06 .01		4-	.07	.05	81.	<b>70</b> .			•	w.		ı
22 8-17 .09 .19 .15 .11 .13 .41 .22 .10 .10 1. 3 17-25 .07 .11 .10 .07 .1 .10 .10 .1 .1 .1 .2 .10 .10 1. 25-37 .02 .03 .06 .01	2 0	79	60-	90.	.22		77	Ľ	•	٠, ٣	C	•
3 17-25 .07 .11 .10 .07 1 25-37 .02 .03 .06 .01 25-37 .02 .05 .01 25-37 .02 .05 .01 2 37-93 .03 .05 .14 .01 2 1-1/2-0 .03 .05 .14 .01 3 14-20 .05 .09 .12 .03 14-20 .05 .09 .12 .03 1 20-27 .03 .08 .09 .03 1 20-27 .03 .08 .09 .03 1 20-27 .02 .04 .08 .03 1 20-27 .02 .04 .08 .03 1 20-27 .02 .14 .20 .04	10	8-7	6	 	5.	) — (	.13	イ	. 22	<b>'</b> —	1 —	• •
2 1-1/2-0 .03 .05 .01 6.13 4.60 -0.4 .04 .02 .12 .03 .27 .76 .69 .46 .41 121		7-2	.07	_;	01.	20.						•
2 1-1/2-0 .03 .05 .14 .01 6.13 4.60 -10-4 .04 .02 .12 .03 .27 .76 .69 .46 .40 2.22 ir 8-14 .15 .28 .18 .12 .18 .41 .46 .26 .20 1.3 14-20 .05 .09 .12 .03 .03 .04 .08 .09 .03 .04 .08 .03 .04 .05 .00 .05 .00 .05 .00 .05 .00 .05 .00 .05 .00 .03 .04 .08 .03 .00 .05 .00 .05 .00 .05 .00 .05 .00 .05 .00 .05 .00 .05 .00 .05 .00 .05 .00 .05 .00 .05 .00 .05 .00 .00		7-5 7-9	.03	.02	.05	50						. 7
2 1-1/2-0 .03 .05 .14 .01 6.13 4.60 -10.4 .04 .02 .12 .03 .27 .76 .69 .46 .40 2.22 ir 8-14 .15 .28 .18 .12 .18 .41 .46 .26 .20 1.3 14-20 .05 .09 .12 .03 .03 .08 .09 .03 .04 .08 .03 .04 .08 .05 .04 .08 .03 .04 .08 .03 .04 .08 .03 .04 .08 .03 .04 .08 .03 .04 .08 .03 .04 .08 .03 .04 .08 .03 .04 .08 .03 .04 .08 .03 .04 .05 .04 .08 .03 .04 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .03 .05 .04 .08 .05 .04 .08 .05 .05 .05 .05 .05 .05 .05 .05 .05 .05												
2 0-4 .04 .02 .12 .03 .51 .41 1. 21ir 4-8 .24 .44 .28 .18 .27 .76 .69 .46 .40 2. 22ir 8-14 .15 .28 .18 .12 .18 .41 .46 .26 .20 1. 3 14-20 .05 .09 .12 .03 .41 .46 .26 .20 1. 1 20-27 .03 .08 .09 .03 .04 .08 .03 .04 .04 .08 .03 .04 .04 .08 .03 .04 .07 .02 .04 .08 .03 .04 .07 .02 .04 .08 .03 .04 .07 .02 .04 .08 .03 .02 .14 .20 .04		-1/2-	.03	.05	71.	<u>.</u>			_	•		•
22   8-14   15   28   18   12   18   41   46   26   20   1.   3   14-20   .05   .09   .12   .03   .09   .03   .09   .03   .04   .09   .03   .04   .04   .08   .03   .04   .05   .04   .08   .03   .04   .05   .04   .08   .03   .05   .04   .08   .03   .05   .05   .04   .08   .03   .05		<b>4</b> α	.04	.05	25 27	٠ ص	7.0	76	5		7	•
3 14-20 .05 .09 .12 .03 1 20-27 .03 .08 .09 .03 2 27-47 .02 .04 .08 .03 1C3 47-73 .02 .14 .20 .04	10	9-1-0	. 15	78	27.		. 18	7.	7		. 20	• •
2 27-47 .02 .04 .08 .03 .04 .04		4-2	50.	9.6	75	9.0						۰.
163   47-73   .02   .14   .20   .04   .02		7-0 7-7	200	0.70	) () ()	200						v-4
	ည်	7-7	.02	71.	.20	0.				.02		9

Table 13, Continued

			0xa1	ate	1	ate-	10		-		P. D.	
Soil	Hor	Depth inches	Fe.	۸۱. ۱.	Dith % Fe.	A1.	Dith. % Fe.	* × *	Leco' c.	*.	Ex Ω%χ	clay
Grayling 16-1 16-1-1 16-1-2 16-1-3 16-1-4 16-1-6 16-1-7	A A B B B B B B B B B B B B B B B B B B	0-1 1-1/2-3 3-7 7-15 15-22 22-44 44-66 66-122	9000000		41-7-7-7-7-7-7-7-7-7-7-7-7-7-7-7-7-7-7-7		.13	.54	2.22 .99 .37 .25	3.16 .31 .12 .04	80.	2-2-
Rubicon 16-2 16-2-1 16-2-3 16-2-4 16-2-5 16-2-6 16-2-7 16-2-7 16-2-8 Ortstein Ave	A1-02 A2 B21ir B22ir B3 C1 C2	0-1 6-10 10-18 18-36 56-120	40.0.0 0.0.0 0.0.0 1.0.0 1.0.0	20.0.00	11. 124. 106. 105. 105. 105.	.03 .03 .07 tr tr tr		.88 .77 .64	2.75 .26 .42 .26 .16	2.17 .38 .17 .16 .06	.21 .03 tr	1-05460
Grayling 21-1 21-1-1 21-1-2 21-1-3 21-1-4 21-1-5 21-1-5	A1 A3 B21 B3 C1	0-1 1-2 2-1/2-7 7-12 12-22 22-68	007	.35 .12 .04		tr .05 .06 tr .01	. 13	1.47	8. 89. 44.	2.79 .70 .29 .12	.23	22.1 22.1 1.4 1.5

able 12, continued

* % Clay	15.3 15.3 10.3 12.9 12.7	2.9 8.2 7.7 231.5	-8 9494V
P.D., Ext. C.	.96 .53 .18	.69	.93 .78 .68
W.B.* C.	10.40 1.58 1.18 .71 .32 .32	10.00 .79 .80 .80 .39	5.80 .08 .73 .18 .06
Lecol %	7.57 1.35 1.35 2.33 3.3	7.99 1.03 1.03 1.43	5. 1.09.7. 26. 4.5. 4.5.
\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	1.22 .98 .72 1.06	1.10	
Pyro. Dith. % Fe.	1.15 1.08 .97 1.45	.58	. 29
ate- . % Al.			.03 tr. .08 .16 .04 .05
Citr Dith % Fe.			
ate % Al.	.06 .43 .30 .23 .17		.01 .33 .17 .01 .05 .12
0xal % Fe.		24. 24. 25. 25. 25. 25.	
Depth inches	0-2 2-6 6-9 9-12 12-18 18-24 28-42	1-0 0-3-1/2 3-1/2-6 6-9 9-13 13-21 21-40	2-0 0-9 0-9 11-15 15-23 23-38 23-38 75-90 90-128
Hor.	02-41 42 821;r 822;r A'2x B'21t C1	02 A2 B21ir B22ir A'2x\$B'21t B'22t	02 A2 B21h B22hir B23 C1 C1 11C2 Avg.
Soi1	Onaway 21-2 21-2-1 21-2-2 21-2-3 21-2-4 21-2-5 21-2-6 21-2-7	Onaway 21-3 21-3-1 21-3-2 21-3-3 21-3-4 21-3-6 21-3-6	Kalkaska 24-1 24-1-1 24-1-2 24-1-3 24-1-4 24-1-5 24-1-6 24-1-7 24-1-9 24-1-9 24-1-10 Ortstein

Table 12, Continued

							4				k	
1:00	; (	1	UXalal	ate	1 1 1	ate-	ب ن	ı -)	[222]	٥	• ]	
100		reptn inches	% d.	% T	ه %−	 	- % - G	× - × - × - × - × - × - × - × - × - × -	ر ان %ور	• × ×	ם × אי	13 18 18
Hiawatha 31-1									;			-1
1-1-1			.02	t	2	.02			$\infty$			•
31-1-2		ထု	90.	.08	.32	.03			. 79			2.2
31-1-3		7	99.	.23	9	.25	2	•	7	2	5	•
	2	Ξ	. 28	9.	す	.27	.35	60.	.≠	7	00.	•
		7-2	<u>0</u>	.27	_	.07		ı	4	$\omega$		•
-	3	5-3	.05	<u>~</u>	0	.03				_		
		3-6	<b>0</b>	· 04	0	<b>.</b> 04						
-		6-0	.03	80	.07	70						
31-1-9	C3	90-110	.02	.07	.07	0.						. 2.
•												
S.			(	1	•				•	•		
	02	- ·	800	.07	- 4.	. 12			5.12	9.10		•
- 7 - 1		ر-0 آ	<u>ئ</u>	بار ا	.35	40.			٠.	j		•
1-2-	21	ۇ.	99.	.58	1.30	<u>∞</u>	1.02	0	_	σ.		•
1-2-		9-1	.35	.57	64.	.43	$\boldsymbol{\omega}$	.93	<u>'</u>	7.	ψ.	•
1-2-	3	7-2	. 12	. 29	.25	%			$\infty$	2		•
1-2-	_	2-2	<b>0</b> .	. 12	17	. 13			.32	_		_
1-2-	-	<b>7-</b> /	.03	90.	91.	<b>•</b> 04						•
_	123×B121	7-0	.05	tr	. 23	.02						•
1-2-	X	9-6	2	tr	.23	tr				· 04		0.9
_	12	62-99	91.	tr	04.	tr						1.0
_	_	9-95	.03	<u>.</u>	<u>6</u>	<u>-</u>						
31-2-12		5-1	.07	tr	84.	tr						
_		5-12	.05	t	.35	ţ						

Table 12, Continued

	:		Oxalat	ate	15.	ate-	Pyro.		-	(	P.D.*	
Soil	Hor.	Depth inches	% <b>₫</b>	%-	Dith Fe	.%-	ith %		Leco'	*. ¤. ×.	E× ۲% د	% <u>-</u>
e -			2 0	6	28	<u>-</u>			7.35	7,00		- ~
1-3-		-1/2-7	0	0	7	.03			.61	. 7.		2.7
1-3-	7	7-11	3	<u>8</u>	5	80.	.43	<b>7</b> 4.	7	<u>. 1</u> 0	.02	•
1-3-		1-2	m (	.5	m	.20	.26	.78	0	47.	. 76	•
31-3-5		23-34	. 24	.26	.22	. ;	<u>. 1</u> 3	.54	2	.43	.32	- ~
1-3		6-1	<b>—</b>	. t.	$\circ$	.03	5	. 20		-	-	Ĵω
1-3-			$\sim$	.36	4	.32	.30	.83	1.06	<b>79</b> .	.89	1.2
McBride 43-1												
m		<b>7-0</b>	01.	0	.23	0			2.37			ı
	2	9	. 15	0	.27	0			•	.7		•
43-1-3 43-1-4	82 i r	97	20 20	- 6	.37	0.0	.32	. 28	٠ <u>٠</u>		. 48	•
	-	12	30	Õ	. 16	t.			<del>.</del>	.12		3.4.
0akville 50-1												
0-1-1	02	1.0	.20	Ξ.	_	tr			$\omega$	10.70		
	A3	0-5	.20	60.	m-	.07		-	2			
$\supset c$	7	<b>P</b> -	207.	17.	4 0	2.5	٠. ٥٠	14.	٠	/*.	. 29 7 - 1	
-1-0	B23	2-2		9	ŌΜ	- 6	<b>^</b>	<b>^</b>	. 26	2.0		
	m	0-2	60.	.07	m	.03			1	80.		
-1-0	<u></u>	4-6	8.	· 04	2	tr				80.		
50-1-8	23   1	47-66	86	<u>.</u>	ه	40.				.07		2°6
-		-		•		•						

Table 12, Continued

			1000	ı	1 + : 0	100	2,70				* 4 0	
Soil	Hor	Denth	סאמומרת		0:1	י טי	Dith	· *	Lecol	*	ж Т	
-	•	inches	%		%	%	· %		)   	· %	; ; ; ;	%
			Fe.	Α1.	Fe.	A1.	Fe.	Α1.	ပံ		ပ	Clay
Omega 52-1												
2-1	A18A2	0-3	.05	0.	8	tr	. 13	. 15	2.35	1,40	94.	3.1
52-1-2	_	, c	22	5	42	17	•	•	' ^	75	•	α,
52-1-3	822	8-12	12	, ~	25	80	81	77	, Y,	50	16	000
72-1-4	1 ~	12-18	0.7	0	71		•	•	, C	α ι C	•	· -
	3.5	200	<u> </u>	90	- α - c	70			. 1.			
ć- 1-7C	) ر	07-01		٠. درون	9 6	•				20.		- I
52-1-6	C2	28-37	.02	9	• 05	٦ ۲				.02		ŗ.
52-1-7	C3	37-43	[	90.	80.	tr						
52-1-8	C4	43-94	<u></u>	.02	.05	tr						7.
ı		<b>I</b>										
McBride 67-1												
	Δ1	0-2	0.5	03	17	70			6.17	6.70		
67-1-2	Δ2	ια. •••	- 2	. +	22	. L			78			•
7,7		,		-		-	-	,		•	(	•
6/-1-3	7	α <u></u> 2	747	71.	٠٠	2 .	.48	.26	9 -	00.	79.	•
67-1-4	_	13-29	.05	-	. 20	.02			. 15	80.		•
67-1-5	A'2xB'21	29-34	. 12	90.	38	Б.				90.		18.6
67-1-6	_	43-73	0	00	38	70				00		
2 - 1 - 2	١_	72 - 111	5	9	,,,					i ) •		•
//0	5		-	3		2						•

Table 12, Continued

as ka 67-2 -1 -2 -3 -4 -5 -5 -6		ב ב נ	?	%	֓֞֞֝֞֝֞֞֝֞֝֓֞֝֓֓֓֓֞֝֞֓֓֓֞֞֞֓֓֞֞֞֓֞֞֞֓֞֞				נ		, ,	
ka 67-2 0 A A A A B B B B B B		inches	₩. •	A .	ĕ. ĕ.		F	۸ ا.	ر الادر	~ C	ر % د	Clay
	. ∇ ∇	3-0	g	5	-	03			7 778			'
		1-4	9.5	50	.0.5	.02				.28		٠,
82 82 82	25	7	90.	t.	<b>70</b>	t	•			· 04		•
മമ	년 ·	77	.23	71.	.34		.58	.28	 8	.77	200	<i>س</i> . م.
۵	.2.r	- c	. 22		2.5	. 24	97.			./2		•
•		ک- <i>لا</i> 2 - د	7	- c	<u>-</u> -	~			~ ~	14,		•
30		7-7	70	7	- 50	. †			. 20	- 6		
C2	1	63-86	0.	77		.02				•		
J		6-1	.02	.03	.05	.0						.2
Avg.			<u>~</u>	<u>ښ</u> ش	.23		. 22	.83	- - - - -	69.	01.1	·.
i cigni chunks 1 Dark Chunks			<u>∞</u>	54.	.23	.15			 82			
nort 74-1												
Α Α	•	_7	60.	0.	. 15	.01			1.28	1.08		1.4
		7	. 12	<b>.</b> 04	<u>∞</u>	t				. 20		_
		7	6	0	. 29	.07		•		.2]		9.
		3-1	. 12	80.	. 28	<b>.</b> 04	.21	. 28		<u>8</u> .	.15	<u>.</u> .
		9-2	. 13	.07		.02						1.2
		6-3	.05	<u>e</u>	91.	<b>.</b> 04				· 04		.7
23		34-52		.03	90.	tr						ئ

\* SCS Beltsville Laboratory results.

1. Leco Carbon Analyzer with induction furnace..

W.B. - Walkley Black.

P.D. - Pyrophosphate-Dithionite extraction. Note;

The second second

Table 13 . Data from soils having ortstein in some horizons

Soil	Horizon	% Total	0xala	ate %
	HOT I ZON	Carbon	Fe	<u> </u>
Rubicon 2-1 2-1-4 2-1-5 2-1-6 2-1-10	B22ir B31 B32 Avg. Ort. Lt. Ort. Dark Ort.	.39 .08 .06 .52 .62	.11 .04 .03 .10 .09	.33 .07 .10 .15 .25
Rubicon 16-2 16-2-5 16-2-8	B3 Avg. Ort.	.16 .30	.03 .16	.02
Kalkaska 24-1 24-1-3 24-1-4 24-1-5 24-1-10	B21h B22hir B23ir Avg. Ort.	.97 .94 .43 .45	.21 .16 .07 .17	.10 .33 .17 .24
Hiawatha 31-3 31-3-3 31-3-4 31-3-8	B21h B22hir Avg. Ort.	1.27 1.01 1.06	.32 .34 .33	.18 .51 .36
Kalkaska 67-2 67-2-4 67-2-5 67-2-6 67-2-11	B21h B22ir B23ir Avg. Ort. Lt. Ort. Dark Ort.	1.18 1.07 .73 1.01 .98 1.18	.23 .22 .15 .18 .18	.14 .32 .41 .38 .58 .44

The aluminum was determined in the same samples as the iron.

Extractable iron and aluminum by three extraction methods plus either total or extractable carbon values for Podzol B horizons Table 14.

		Total	Carbon*	Plus	F × F	Fytractable Carbon*	21.10
Soil	Horizon	0xalate Fe + Al	Cit-Dit.	Pyro-Dit.	Oxalate Fe ± A1	$\Box$	17
Rubicon 2-1-3 2-1-4	821ir 822ir	၂ ထထ	69.1	2.37	ار	1.17	1.83
Munising 7-1-3 7-1-4	B21hir B22ir	4.08 2.69	4.12 2.65	4.64	3.34 1.98	3.45 1.93	3.91 2.35
Vilas 7-2-3 7-2-4	821ir 822ir	1.41	1.28	2.20	1.06	.93	1.85
Omega 7-3-2 7-3-3	821 822	. 50	. 78	1.20	.388	.36	86.98
Rousseau 7-4-3 7-4-4	821ir 822ir	1.37	1.15	1.72	1.08	.50	1.43
Grayling 16-1-4	B22	.37	15.	.92	.22	.36	.77
Rubicon 16-2-3 16-2-4	821ir 822ir	.83 .54	. 74°.	1.51	.62 .46	.355	1.30

Table 14, Continued

Soil	Horizon	Total	1 Carbon* Plus	lus	Extrac	Extractable Carbon*	on* plus
		Oxalate Fe + Al	Cit-Dit. Fe + Al	Pyro-Dit. Fe + Al	Oxalate Fe + Al	Cit-Dit. Fe + Al	Pyro-Dit. Fe + Al
Grayling 21-1-3	821	.77	.87	2.12	.57	.67	1.92
Onaway 21-2-3 21-2-4	821ir 822ir	2.34 1.50	3.16	3.74 3.01	1.93	2.75 1.98	3.33
Onaway 21-3-3 21-3-4	821ir 822ir	1.53	1.65	2.53	1.13	1.25	2.09
Kalkaska 24-1-3 24-1-4	821h 822ir	1.28	1.36	2.37	1.09	1.17	2.18
Hiawatha 31-1-3 31-1-4	B21hir B22ir	2.64 2.14	2.90 2.14	4.28 2.86	2.45	2.71	4.09 2.44
Munising 31-2-3 31-2-4	B21hir B22ir	4.40 2.63	4.65 2.64	5.28	3.46	3.72 2.04	4.34
Hiawatha 31-3-3 31-3-4	821h 822ir	1.77	1.92	2.14	1.45	1.60	1.82 1.80
McBride 43-1-3	82ir	1.17	1.23	1.39	98.	.92	86.

Table 14, Continued

Soil	Horizon	Tot	Total Carbon* Plus	Plus	Extract	Extractable Carbon* plus	n* plus
		Oxalate Fe + Al	Cit-Dit. Fe + Al	Pyro-Dit. Fe + Al	Oxalate Fe + Al	Cit-Dit. Fe + Al	Pyro-Dit. Fe + Al
0akville 50-1-3 50-1-4	B21 B22	96.	1.06	1.31	.51	.81	1.06
0mega 52-1-3	B22	.80	89.	76.	.61	64.	. 78
McBride 67-1-3	B2ir	1.60	1.67	1.90	1.15	1.23	1.46
Kalkaska 67-2-4 67-2-5	B21h B22ir	1.53	1.64	2.04 1.98	1.32	1.41	1.81
Eastport 74-1-4	B21	64.	09.	77.	.36	.47	79.

Total carbon was determined by an induction furnace (Leco carbon Analyzer) Extractable carbon was determined in the Pyrophosphate-Dithionite extracts. Note\*:

Ratios of extractable iron plus aluminum by three extraction methods, plus either total carbon or extractable carbon\* to total clay contents Table 15.

							-	
Soil	Horizon	Profile	0xa1a	late	Citrate-d	Citrate-dithionite	ryropno dithion	spnate- ite
Series		Number	% T.C.+ %Fe & Al	%Ext** C+ %Fe & Al	% T.C*+ %Fe & Al	%Ext <b>#</b> C.+ %Fe & Al	%T.C. + %Ext. %Fe & Al % Fe	%Ext. C"+ % Fe & Al
Rubicon	821ir 822ir	2-1-3 2-1-4	.50	.43	.45	.34	0†°	.50
Munising	821hir 822ir	7-1-3 7-1-4	.38 4.5.	.31	.38	.32	.39	.37
Vilas	821ir 822ir	7-2-3 7-2-4	.53	. 53	.63	.32	1.10	210
Omega	B21 B22	7-3-2 7-3-3	.36	.28	.30	.21	77. 97.	
Rousseau	821ir 822ir	7-4-3		.51	.54	.33	.81	.56
Grayling	B21 B22	16-1-3	.28	61.	.33	.24	.57	.51
Rubicon	821ir 822ir	16-2-3 16-2-4	.36	.31	.29	<u>~</u>	.50	. 43
Grayling	B21 B22	21-1-3 21-1-4	.36	.27 Insu	.41 nsufficient D	.32 Data	1.01	.39
Onaway	821ir 822ir	21-2-3 21-2-4	.15	.12	.20	. 17	.23	.21

Table 15, continued

Soil Series	Horizon	Profile Number	0xalate % T.C.+ %E %Fe & Al %F	%Ext: C+ %Fe & Al	Citrate-d % T.C*+ %Fe & Al	itrate-dithionite T.C*+ %Ext**C.+ Fe & Al %Fe & Al	Pyroph dithio %T.C. + %Fe & Al	rophosphate- thionite + %Ext: C.+ Al %Fe & Al
Onaway	821ir 822ir	21-3-3 21-3-4	. 18	.13 51.	.20	.15	.30	.30
Kalkaska	821h 822hir	24-1-3 21-1-4	.79	.35	. 73	.38	1.20	.70
Hiawatha	B21hir B22ir	31-1-3	.38	.36	.93	. 74	.63	.60
Munising	821hir 822ir	31-2-3 31-2-4	.61	95.	99. 99.	.51	.73	09.
Hiawatha	821h 822hir	31-3-3	.49	1.07	.53	44.	1.36	.50
McBride	B2ir	43-1-3	.20	.15	.21	91.	.24	91.
Oakville	821 822	50-1-3 50-1-4	.26	61.	. 28	.22	.33	.29
Omega	B22	52-1-3	.38	.22	.34	.17	.34	. 28
McBride	B2ir	67-1-3	.22	.17	. 23	.17	. 26	.20
Kalkaska	821h 822hir	67-2-4 67-2-5	.40	1.09	.42 1.22	1.08	1.54	1.38

Table 15, continued

1:00	1	Drof: 10	Oxalate	Citrate-dithionite	thionite	Pyrophosphate	osphate-
Series		Number	%T.C. + %Ext. C+ %Fe & Al %Fe & Al	% T.C.*+ %Fe & A1	%Ext." C.+ %Fe & Al	%T.C. + %Fe & A1	%Ext** C.+ 1 % Fes Al
Eastport	B21	74-1-4	.37	.38	.36	.59	64.

\*Total carbon was determined by a Leco Carbon Analyzer which utilizes a high temperature induction furnace.

\*\* Extractable carbon was determined in the pyrophosphate-dithionite extracts by the standard SCS procedure.

Table 16. Ignition test results on B and C horizons

	***************************************										
Soil Profile	B. hor. field moist hue	B. hor. ignited moist hue	Change in hue after ignition	C. hor. field moist hue	C hor, ignited moist hue	Change in hue after ignition	lgnited hue, B redder than C	C.D. Ext. %Fe	Oxalate Ext. %Fe	P.D. Ext. Fe	
Rubicon 2-1	5YR	5YR- 2.5YR	1/2	7.5YR	5YR	-	yes	644.	.259	. 22	
Munising 7-1	5YR	2.5YR	_	5YR	5YR	0	yes	.828	.611	79.	
Vilas 7-2	5YR	5-2.5YR	1/2	5YR	5YR	0	yes	.388	. 265	.38	
Omega 7-3	5YR	5-2.5YR	1/2	5YR	5YR	0	yes	. 268	91.	.24	2
Rousseau 7-4	5YR	5-2.5YR	1/2	5YR	2.5YR	_	ou	.281	.238	.27	.13
Grayling 16-1	7.5YR	5YR	_	10YR	5YR	2	OL	.265	160.	. 22	
Rubicon 16-2	5YR	2.5-5YR	1/2	10YR	5YR	2	yes	.244	.155	.21	
Grayling 21-1	7.5YR	5YR	_	10YR	5YR	2	o O	.268	104	.22	
Onaway 21-2	5YR	2.5YR	_	7.5YR	5YR	_	yes	1.154	.537	1.15	
Onaway 21-3	5YR	5YR	0	7.5YR	5YR	_	o O	.537	.405	.67	
Kalkaska 24-1	5YR	5YR	0	10YR	5YR	2	OL OL	.314	.210	.29	
Hiawatha 31-1	5YR	2.5YR	_	7.5YR	5YR	_	yes	.920	999.	1.24	
Munising 31-2	2.5YR	2.5YR- 10R	1/2	2.5YR	10R	_	Ou	1.303	.658	1.02	

Table 16, continued	panu									
Soil Profile	B. hor. field moist hue	B. hor. ignited moist hue	Change in hue after ignition	C. hor. field moist hue	C.hor. ignited moist hue	Change in hue after ignition	lgnited C hue, B E redder % than C	X X t.	Oxalate P.D. Ext. Ext. %Fe Fe	P.D. Ext. Fe t
Hiawatha 31-3	5YR	2.5YR	_	7.5YR	5YR	_	yes	.570	.324	.43
McBride 43-1	5YR	5YR	0	C horizo	C horizon not available	ilable		.371	.257	.32
Oakville 50-1	7.5YR	5YR	_	10YR	7.5YR	_	yes	.425	.202	.36
Omega 52-1	7.5YR	5YR	_	5YR	5YR	0	OU	.426	.220	.18
McBride 67-1	5YR	5YR	0	5YR	5YR	0	OU	.515	614.	84.
Kalkaska 67-2	5YR	2.5YR	_	10YR	7.5YR	_	yes	.343	.234	÷ 85·
Eastport 74-1	10YR	2.5YR	~	10YR	7.5YR	_	yes	. 288	.095	.21

A Rousseau subhorizon below the main spodic horizon was also ignited to find out what the color change might be. Horizon 7-4-4-. 5YR moist B: 2.5YR ignited. Two lower Kalkaska (24-1) horizons below the main spodic B horizon were also ignited. The results showed no difference between the field moist and ignited moist hues. Two lower horizons from the Kalkaska (67-2) profile were also ignited. There was no difference between the field moist and ignited moist hues. Note:

In this test samples were ignited at  $525^{\circ}\mathrm{C}$ . for 3 hours to burn off all of the organic

Placement of Profiles studied into the comprehensive classification system using current and some proposed revised criteria Table 17.

Soil	Horizon	Proposed Revi	Revised		Current		
- -	color	Oxalate	Citdit.	Pyro-dit.	Criteria**	Ouick Test	
(Vilas⊁** Rubicon 2-l	5YR3/4	Entic Haplorthod*	Same	Entic Haplohumod	(Entic Haplorthod) Entic Haplohumod	10YR6/3	
Munising 7-1	5YR3/3	AFic Fragiorthod*	Same	Same	Alfic Fragiorthod	10YR4/4	
Vilas 7-2	5YR4/4	Entic Haplorthod*	Same	Same	(Entic Haplorthod) Entic Haplohumod	10YR7/1	
Omega 7-3	5YR4/4	Typic Udipsamment*	Same	Same	(Spodic Udipsamment) Typic Udipsamment	10YR8/1	
Rousseau 7-4	5YR4/4	Entic Haplorthod*	Entic Haplo- humod	Entic Haplor- thod	(Spodic Udipsamment) Entic Haplohumod	10YR7/2	
Grayling 16-1	7.5YR4/4	Typic Udipsamment*	Same	Same	Typic Udipsamment	10YR8/1	
Rubicon 16-2	7.5YR4/4	Entic Haplohumod≝	Spodic Udipsa- mment	Entic Haplo- humod	Entic Haplohumod (Entic Haplorthod)	10YR8/1	
Grayling 21-1	7.5YR4/4	Typic Udipsamment*	Same	Same	Typic Udipsamment	10YR8/1	
Onaway 21-2	5YR3/4	Alfic Haplorthod*	Same	Same	Alfic Haplorthod	10YR5/6	

Table 17, continued

Soil	Horizon	Proposed Revised Criteria*†	vised a* <b>†</b>		Current	
	color	0xalate	Citdit.	Pyro-dit.	Criteria**	Quick Test
Onaway 21-3	5YR3/4	Alfic Haplohumod	Same	Alfic Haplorthod	Alfic Haplorthod*	10YR6/3
Kalkaska 24-1	5YR2/2	Entic Haplorthod*	Same	Same	(Typic Haplorthod) Entic Haplohumod	7.5YR4/4
Hiawatha 31-1	5YR2/2	Typic Haplorthod*	Same	Same	Typic Haplorthod	5YR3/4
Munising 31-2	2.5YR2/2	Alfic Fragiorthod*	Same	Same	Alfic Fragiorthod	5YR3/4
Hiawatha 31-3	5YR2/2	Typic Haplorthod*	Same	Same	(Typic Haplorthod) Typic Haplohumod	5YR3/4
McBride 43-1	5YR3/4	Alfic Fragihumod	Same	Same	(Alfic Fragiorthod)" Alfic Fragihumod	10YR6/3
Oakville 50-1	7.5YR4/4	Entic Haplohumod	Entic Haplor- thod	Same	(Spodic Udipsamment) Typic Udipsamment*	10YR7/1
Omega 52-1	7.5YR4/4	Typic Udipsamment	Typic Udipsa- mment	Same	(Spodic Udipsamment) Typic Udipsamment*	10YR7/2

Table 17, continued

		Proposed Re	Revised			
Soil	Horizon color	Criteria#† Oxalate Ci	ia*† Citdit.	*† Citdit. Pyro-dit.	Current Criteria**	Quick Test
McBride 67-1	5YR3/2	Alfic Fragihumod	Same	Same	(Alfic Fragiorthod)" Alfic Fragihumod	10YR5/4
Kalkaska 67-2	5YR3/2	Entic Haplorthod	Same	Same	(Typic Haplorthod) Entic Haplorthod*	5YR3/4
Eastport 74-1	7.5YR5/4	Spodic Udipsamment	Same	Same	(Entic Haplorthod) Spodic Udipsamment*	10YR7/1

\*†The proposed revised criteria are listed in the section on Use of Chemical Data to Classify Soils.

\*\*The names in parentheses are the January 1968 placements of these series, where different than that for this profile.

\*\*\*Proposed classification for this series in Michigan.

"This is proposed as an Alfentic Fragiorthod subgroup.

\*Proposed placement into the classification system.

Table 18. Data on Southern Michigan soils\*

Soil	Horizon color	Citdit. % Fe	Ext. % Al	Total % C	Total % Fe+A1+C.	% Clay	Ratio	Ratio Classification
Eastport	10YR6/6	440.	.026	.120	.190	. 24	. 79	Spodic Udipsa- mment
Rubicon	7.5YR5/6	.102	.061	. 180	.343	94.	.73	Spodic Udipsa- mment
Kalkaska	7.5-5YR4/6	.241	. 286	.770	1.297	1.40	.90	Entic Haplohumod
Blue Lake I	5YR2/2	.284	Ξ.	.550	.945	3.80	.25	Alfic Haplorthod
Blue Lake II	5YR2/2	.540	.290	.290 1.280	2.110	04.9	.33	Alfic Haplorthod

\* This data was taken from Franzmeier's study of Podzol Formation (29)

The total carbon values are by dry combustion.

The requirements for citrate-dithionite extraction spodic horizon are Fe = 0.31% and total Fe+Al+C = 0.8%

The Eastport and Rubicon profiles would today be classified as DeerPark series, and the Kalkaska would be Rubicon.

Data on Upper Michigan soils studied by Messenger (48) Table 19.

Soil	Profile Number	Profile Horizon Number color	Citdit. %Fe	it. Ext. % Al	Total % C	Total %Fe+Al+C	% Clay	Ratio Total Clay	Classification
Eastport	A2	10YR5/6	.325	.037	.422	. 78	.76	.76 1.02	Spodic Udipsamment
Eastport	A3	10YR5/6	.230	.032	.295	.56	. 78	.71	Spodic Udipsamment
Rubicon	81	5YR4/8	.500	.037	.452	66.	1.50	99.	Entic Haplorthod
East Lake	. B2	5YR3/6	.518	.077	.458	1.05	4.01	.25	Entic Haplorthod
Rubicon	C1	7.5YR4/4	.455	. 283	.655	1.39	3.17	44.	Entic Haplorthod
Kalkaska	C2	5YR2/3	.613	.249	1.957	2.82	4.68	09.	Typic Haplorthod
.Ka 1 kas ka	01	5YR2/2	. 588	.085	.673	1.35	4.49	.30	Entic Haplorthod

The proposed correlation of these soils is as follows: Eastport, A2, A3 no change Rubicon Bl and C1 profiles as Vilas. Kalkaska C2 as Hiawatha. Kalkaska D1 no change. The total carbon value was determined by Allison's method. Note:

Fe = 0.31%The citrate-dithionite extraction requirements are as follows: Total Fe+Al+C = 0.8%.

# APPENDIX IV

The Canadian System for Classifying Podzolic Soils

This section was extracted from the Report of the Sixth Meeting of the National Soil Survey Committee of Canada, held at Laval University, Quebec, October 18-22, 1965.

### Podzol Great Soil Group

Soils with organic surface horizons, with light colored eluviated horizon (Ae) and with illuvial horizons (Bfh, and Bf) of higher chorma in which organic matter and sesquioxides are the main accumulation products. Under virgin conditions the Ae is more than 1 inch thick and the upper 4 inches of the B horizon contain an average of less than 10% of organic matter. The organic matter to oxalate Fe ratio is less than 20 and the oxalate Fe + Al content (oxalate extraction) in the upper 4 inches exceeds that of the C horizon by 0.8% or more. The solum generally has a low degree of base saturation, based on permanent charge, and the B horizons have a high pH dependent charge. sandy Podzols may have moderate to high base saturation. The color of the B horizon generally has values of 3 or more and chromas of 4 or more. The difference in color value or chroma between the Ae and B should be 2 or more.

The Bfh, Bh, or Bf if present, may also contain more clay than the A2 or C horizons (possibly due to infiltration or translocation with organo-mineral complexes). The clay is not, or is only very weakly, oriented and does not form clay skins. Although the increases of clay in the B may

be as great as those required for textural B horizons, due to a lack of orientation they do not meet the requirements of textural B horizons. Thin, involute, hard, impervious dark reddish ironpans are absent. A fragipan may underlie the Bf horizons.

### Orthic Podzols:

Podzol soils with organic surface horizons, with light colored eluvial horizons, more than I inch thick and with friable Bfh and Bf horizons, generally having a chroma of 4 or more. The difference in chroma or value between the Ae and Bfh or Bf is 2 or more. A thin Bhf horizon may be present but the average organic matter content of the upper 4 inches of B is less than 10%. In the Bfh and Bf horizons Fe + Al (oxalate extraction) exceeds that of the C horizon by about 0.8% or more. The Bfh horizon may contain more clay than the Ae or C horizons but the clay is not oriented and does not form clay skins. The most prominent accumulation of clay occurs immediately below the Ae in the horizon of greatest organic matter content and sesquioxide accumulation. Some mottling may occur in the lower B horizon, particularly if the latter is underlain by a fragipan.

### Podzo Regosol Great Group

Well and imperfectly drained soils that have light colored eluvial horizons (Ae) more than I inch thick and

weak illuvial horizons (B) containing insufficient accumulations of sesquioxides, clay or organic matter to meet the requirements of the Podzolic Order. The parent materials of these soils is coarse to moderately coarse textured. Organic surface horizons (L-H) are usually present in the virgin soils but seldom exceed a few inches in thickness. Weak or thin Ah horizon may also be present.

#### Arenic Podzo Regosols

Podzo Regosols with free iron and aluminum as the main accumulation products in the B horizon but less than that required for the Podzol Great Group. That is, the oxalate extractable (Fe%Al) is less than the 0.8%. These soils strongly resemble Podzols in appearance except the B horizon are usually lower in chroma. Also they usually have less acidic sola and higher base saturation than the Podzols. These Podzo Regosols have only been found on sands having a low amount of weatherable minerals. They occur in many parts of Canada.

## <u>Bisequa Podzol</u>

Soils with Podzol sola which have developed in the Ae horizons of Gray Wooded or Gray Brown Podzolic soils and which are underlain by a textural Bt horizon at a depth of 36 inches or more, or at a shallower depth (18-36 inches)

depending on the relative degree of Podzol and textural B development. The Podzol development should at least meet the minimal requirements of the group (difference between Ae and B should have a value and chroma of 2 or more, or difference in Fe and Al (oxalate extractable) between the B and C should be about 0.8% or more), and the Bt should meet the requirements of the textural B.

Soils in which the development of the upper solum is too weak to meet the requirements of Podzols, but with a Bt horizon as defined, may be classified as Bisequa Gray Wooded; while soils in which the Podzol sequence meets the requirements of the group but in which the lower B does not meet the requirements of the textural B may be classified with the other appropriate Podzol subgroup. Soils having the general appearance of Podzols but in which neither the Podzol nor the textural B meet the respective requirements, as defined, should be classified in the Brunisolic or Regosolic Order.

## Bisequa Gray Wooded

Gray Wooded soils in which a Podzol sequence of horizons has developed in the Ae of the Gray Wooded soil and which is underlain by a continuous Bt horizon.

The development of the Podzol sequence relative to the development of the Bt may vary greatly in intensity and in depth, resulting in a range of profiles that resemble the Brunisolic Gray Wooded soil on one hand and the Bisequa Podzol on the other.

The following arbitrary limits are suggested as a guide for the separation of the two subgroups. All soils in which the depth to a well developed Bt is less than 18 inches should be classified as Bisequa Gray Wooded. All soils in which the depth to a Bt is greater than 36 inches should be classified as Bisequa Podzols. In cases where the depth of the Bt is between 18 and 36 inches, the classification is done as explained under Bisequa Podzol.

Coarse textured soils with profiles resembling Bisequa Gray Wooded but in which the Podzol sequence does not meet the minimal requirements of a Podzol should be classified as Brunisoloc Gray Wooded; if both the Podzol sequence and the textural B do not meet the respective requirements, the soil should be classified in the Brunisolic or Regisolic order.

Criteria for Bh Horizons.

- 1. Contains more than 2% organic matter.
- The organic matter to oxalate extractable Fe ratio is 20 or greater.

- 3. Horizon chroma less than 3 (moist).
- 4. Difference in oxalate extractable Fe + Al in B minus those in the C is less than 0.8%.

### Subdivisions:

Bf - less than 5% organic matter

Bfh - from 5 to 10% organic matter

Bhf - more than 10% organic matter

### Modifier:

j Modifier used when a horizon possesses some qualities of a Bh or Bf horizon but does not actually qualify. eg. Bfj or Bhj.

m A horizon slightly altered by hydrolysis, oxidation and/or solution to give a change in color and/or structure. The suffix is used only with B to denote a B horizon that is greater than chroma by I or more units than the parent material, or that has granular, blocky or prismatic structure without evidence of strong gleying, and that has oxalate extractable Fe + Al less than 0.8%. It may not be used under an Ae horizon but may be used under an Aej horizon. This rule distinguishes it from a Bfj horizon.

While changes may have been made since 1965 the Michigan soils in this study are classified according to the criteria listed above.

### Acid Brown Wooded Great Group

Brunosolic soils with organic surface horizons, with a Bf or Bm horizon and a moderately to strongly acid solum, but without a distinct mineral-organic surface horizon.

Light colored eluvial horizons up to 1 inch thick may be present. The chroma, the organic matter content and the oxalate extractable iron and aluminum of the Bf or Bm horizons decrease with depth. The sola have pH values (in water) ranging generally from 4.5 to 6.0 and the base saturations (determined by NaCl extraction) range from 65 to 100 percent. The parent materials are usually acidic.

Earthworms are invading some Acid Wooded soils and under their action the upper mineral part of the solum is incorporated into the organic surface to form a distinct Ah horizon. Where such conditions are found these soils may be included with the Acid Brown Forest Great Group.

The Acid Brown Wooded soils appear to represent a stage of soil development between the Regosol and the Podzol.

### Degraded Acid Brown Wooded

Soils with Ae horizons less than I inch thick or Aej several inches thick and with Bf, Bfh, or Bm horizons.

# Summary of Criteria for Canadian Horizon Designations

Criteria for Bf horizons:

- 1. Chroma of 3 or more
- 2. Oxalate extractable Fe & Al from the B horizon minus the oxalate extractable Fe + Al in the C horizon greater than 0.8%
- Organic matter to oxalate extractable Fe ratio is less than 20.

Canadian classification criteria and its application to Podzol B horizons studied Table 20.

Soil and horizon	Ratios Fe + Al	ios 0M * Fe <20	Ae Hor.? *1"	2-5% OM. or more	Horizon	Classification
Rubicon 2-1-3	OL .	yes	yes	less	Bfj	Arenic Podzo Regosol
Munising 7-1-3	yes	yes	yes	yes	Bf	Bisequa Podzol
Vilas 7-2-3	Ou	yes	yes	less	Bfj	Arenic Podzo Regosol
Omega 7-3-2	Ou	yes	OL	less	(8)	Degraded Acid Brown Wooded
Rousseau 7-4-3	OL	yes	yes	less	Bfj	Arenic Podzo Regosol
Grayling 16-1-3	OL	yes	OL	less	Bfj	Degraded Acid Brown Wooded
Rubicon 16-2-3	OL	yes	yes	less	Bfj	Arenic Podzo Regosol
Grayling 21-1-3	Ou	yes	O U	less	Bfj	Degraded Acid Brown Wooded
Onaway 21-2-3	Ou	yes	yes?	yes	Bfj?	Bisequa Gray Wooded

Table 20, continued

	Rai	Ratios	Ae	2-5% OM.		
Soil and horizon	Fe + A1 >0.8%	0M <u>+</u> Fe -20	Hor.? >1"	or more	Horizon	Classification
Onaway 21-3-3	O L	yes	yes	less	Bfj	Bisequa Gray Wooded
Kalkaska 24-1-3	o c	yes	yes	less	Bfj	Arenic Podzo Regosol
Hiawatha 31-1-3	yes	yes	yes	yes	Вf	Orthic Podzol
Munising 31-2-3	yes	yes	yes	yes	Bf or Bfh/Bt	Bisequa Podzol
Hiawatha 31-3-3	yes	yes	yes	less?	Вf	Orthic Podzol
McBride 43-1-3	ou	yes?	yes	less	Bfj?/Bt	Bisequa Gray Wooded
0akville 50-1-3	ou	yes	OL	less	Bfj?	Orthic Acid Brown Wooded
Omega 52-1-2	ou	yes	OL	less	(8)	Degraded Acid Brown Wooded
McBride 67-1-3	ou	yes	yes	less	Bfj/Bt	Bisequa Gray Wooded
Kalkaska 67-2-4	ou	yes	yes	yes?	Bfj	Arenic Podzo Regosol
Eastport 74-1-3	ou	yes	yes	less	Bfj?	Arenic Podzo Regosol