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EXTRACTABILITY OF CARBON, IRON AND ALUMINUM FROM SPODIC HORIZONS OF REPRESENTATIVE MICHIGAN SPODOSOLS, USING VARIOUS CHELATING AGENTS

By

Massoud Hakimian

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ABSTRACT

EXTRACTABILITY OF CARBON, IRON AND ALUMINUM FROM SPODIC HORIZONS OF REPRESENTATIVE MICHIGAN SPODOSOLS, USING VARIOUS CHELATING AGENTS

By

Massoud Hakimian

Soil samples of the spodic B horizons of some representative Michigan Spodosols, as well as, the A horizons, the argillic horizon, ortstein and the fragipan were subjected to extraction with different inorganic and organic chelating agents of varying pH. The amounts of extractable iron and aluminum were determined in the soil extracts. The amounts of extractable carbon were determined from the difference between the total carbon of the soil samples before and after extraction.

Statistical analysis of the extraction data reveals that the 0.1M Na_2-NTA, 0.1M $Na_4P_2O_7$ and 0.1M Na_2-EDTA extraction procedures for Fe produce decreasing amounts with significant differences between them. Na_5-DPTA, at pH 12, resulted in the precipitation of Fe in the soil extract.

The 0.1M Na_5-DPTA and 0.1M Na_2-NTA extractable Al were comparable. However DPTA extractable Al results were significantly higher than for 0.1M Na_2-EDTA and 0.1M Na_4-P_2O_7. The 0.1M Na_2-NTA is suggested to be a suitable Al extractor.

The low pH solutions (EDTA and NTA) were good extractants for carbon. However, EDTA results were significantly greater than for the other extractants. NTA produced comparable results with the high pH extractants.

In general the 0.1M Na_2-NTA offers greater promise as an extractant of Fe, Al and C, and hence as a classification tool, than extractants which were equally or more "efficient" in extracting Al (DPTA) or C (EDTA).

The amount of extractable iron and aluminum is the lowest in the poorly drained Kinross pedon. However, the maximum Fe accumulation occurs in the somewhat-poorly to moderately well-drained AuGres-Croswell member of a sandy toposequence. Extractable aluminum maximum occurs in the somewhat-poorly drained Saugatuck-AuGres. The magnitude of the Al complex extracted by the chelating agents usually exceeded the corresponding amounts of iron. The lowest extractable C occurred in the well-drained member of the drainage catena, namely Croswell-Graycalm, while the highest amount of the extractable carbon was found in the somewhat poorly-drained Saugatuck-AuGres.

The amount of illuvial Fe, Al and C increases with the increase in the pedogenic development of the spodic horizons of the well-drained Spodosols studied. Thus the weakest spodic B_s (Omega and Eastport) contained the lowest amount of extractable Fe, Al and C, while the stronger Hiawatha

and Munising exhibit the highest amount of extractable Fe, Al and C.

The accumulation products of the spodic B horizon are used as a chemical criteria for classification of the Spodosols. It is suggested that the currently used ratio of % extractable Fe and Al over % clay should be reduced from .15 to .10 to include most Spodosols (AuGres-Croswell, Croswell-Graycalm and Munising). It is also suggested that the required ratio be lowered to 0.04 for the well-drained, fine-textured as well as the poorly-drained Spodosols (Onaway and Kinross). Furthermore, the data obtained in this study indicate that the % total carbon, % extractable Fe and % extractable Al over % clay, the previous criterion for the classification of Spodosols, provides a better estimate of the illuvial material of the spodic B horizon for classification purposes in these Spodosols.

TO THE MEMORY OF MY FATHER

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INTRODUCTION

Spodosols (podzols) are soils which are characterized by a diagnostic subsurface horizon, the spodic horizon. The spodic horizon is one in which a relatively high content of illuvial organic matter and sesquioxides occurs. These substances form an active amorphous material with a high exchange capacity, large surface area, and high water retention property.

In border-line cases where the morphological features are so weakly expressed as to prevent the identification of such soils in the field by the soil scientist, the chemical criteria based on the laboratory measurements of organic material and sesquioxides would be of much value in identification and classification of these soils.

One of the theories concerning the formation of spodic horizons postulates the mutual flocculation of positively charged sesquioxide colloids and negatively charged organic colloids. Other theories suggest the changes in redox-potential or in pH as a primary cause for organic material and sesquioxides flocculation. The more recent and accepted theories indicate the involvement of a chelation

reaction and electrostatic bonds in the association between organic matter, iron, and aluminum. Such compounds are soluble and are immobilized when: the concentration of sesquioxide reaches a critical level, or the hydrolysis of the organic metal complex is induced by a change in pH, or there is biological destruction of organic ligands.

A large number of organic compounds with appropriate electron-donor groups capable of chelating the metals can be used to extract the organic matter, iron and aluminum from the immobilized amorphous material of the spodic horizon.

The objectives of this study are as follows:

(1) To study variations of the extractable illuvial organic carbon, iron and aluminum contents of the spodic horizon with different inorganic and organic aqueous chelating agents and their relationship to the pH of the extraction.

(2) To investigate the extractability of illuvial organic carbon, iron and aluminum of the spodic horizon as affected by the position of the ground water (in a toposequence of Spodosols) and the degree of spodic horizon development (in well-drained Spodosols with varying degrees of spodic horizon development).

(3) To evaluate the relative suitability of the various extracting agents in the characterization and classification of the pedons studied according to the new Soil Taxonomy, 1970.

LITERATURE REVIEW

Illuvial Spodic Horizon

The early Western European observers of ortstein and its subsequent recognition by Russian workers brought about the idea of the downward translocation of substances from the upper layers of the soil to lower layers. In general, the transference was thought of as occurring in solution. Pavlinov in 1887 suggested that the movement of clay particles occurs in solution (Muir, 1961). However, the more general concept of illuviation in the pedological sense was suggested by Vysotzky in 1889, who defined the illuvium as the material washed out of the surface soil and deposited below to form a definite horizon of accumulation, such as the illuvial horizon (Muir, 1961). Zakharov in 1906 advocated the recognition of the illuvial horizon as a part of the podzolic profile and proposed that the following letters should symbolize the various horizons: A, upper humus horizon; B, transitional or podzolic-eluvial horizon; C, illuvial (ortstein) horizon; D, parent material. This particular usage of symbols continued among many Russian workers until about 1930, when the form earlier proposed by Glinka: A, eluvial; B, illuvial; C, parent material, with the addition

of numeral subscripts for subdivisions, became the standard (Muir, 1961).

Stobbe and Wright (1959) give a more definite distinction between the illuvial horizon and other horizons of a characteristic podzol soil in the following sequence where A_0 or O_2 horizon identifies the organic surface layer. Directly under the surface organic horizon is a light-colored eluvial A_2 horizon which has lost relatively more sesquioxide than silica. The A_2 horizon rests over a dark-colored illuvial horizon in which the organic material and sesquioxides leached from the A_2 horizon have accumulated.

The new comprehensive system of soil classification developed by the U.S. Department of Agriculture (Soil Taxonomy, 1970, unedited) defines spodic horizons as diagnostic sub-surface illuvial horizons which are characteristic features of most Spodosols (podzols) and are developed from medium to coarse-textured material under humid environment and forest or heath vegetation. These horizons contain active amorphous materials composed of organic matter and aluminum, with or without iron. The word "active" is used to describe material having high exchange capacity, large surface area, and high water retention.

Theories of Organic Matter and Sesquioxides Translocation and Accumulation in Subsoil

The mechanisms by which the organic matter and sesquioxides, particularly the latter, have been removed from the A horizons and deposited in the illuvial B horizon, have been of most concern in the process of podzolization. However, the podzolization process will not be taken to mean only those reactions involved in mobilization and subsequent deposition of sesquioxides in the pedo-sphere. Rather, it will be necessary to consider the sum total of all the reactions apparently associated with the development of the kind and sequence of soil horizons described by Stobbe and Wright as characteristic of podzols.

In general, there are three groups of reactions cited as being contributors to podzolization. Mattson's (1931, 1934, 1942) theories on isoelectric weathering, while appearing quite sound chemically, require a pH gradient with depth in the soil which is not commonly found in podzols. Before this mechanism is lightly dismissed, however, consideration should be given to the mechanism as being reasonably important in the earliest stages of podzol development when there may be a sufficient pH gradient in the profile.

A more widely accepted reaction used to explain podzolization has been the citation of the significant difference in solubilities of the reduced versus the oxidized sesquioxides of iron. Link (1958) reports various solubility

product (K_{sp}) values for ferrous oxide (FeO) and ferrous hydroxide $Fe(OH)_2$ ranging from $7x10^{-13}$ to $4.5x10^{-21}$. The K_{sp} figures most accepted by Link (ibid.) are $8x10^{-16}$ at 25°C or a solubility of about $1.5x10^{-5}$ moles/liter at 25°C. Solubility products for ferric oxide (Fe_2O_3) and ferric hydroxide $Fe(OH)_3$ are reported by Link (ibid.) as being $3.16x10^{-38}$ or $3.2x10^{-36}$ and solubilities as being from 3 to $3.4x10^{-10}$ moles/liter.

To substantiate this mechanism of reduction to the ferrous state in the A horizon with a subsequent oxidation to cause precipitation in the B horizon, it must be shown that such reactions are indeed active in soils that show advanced podzol morphology. McKenzie and Erickson (1954) made redox-potential measurements in two podzol profiles during one summer and found slight but definite evidence of higher oxidation potentials in the B horizon than in the A horizon. A later paper by McKenzie, et al. (1960) reported redox potentials for a two year period and further confirmed that B_{ir} horizons of podzols have a higher oxidizing potential than do either overlying or underlying layers. The cause of the observed variation in redox potentials between the A, B and C horizons was further examined by McKenzie, et al. (ibid.). They found that ferric citrate oxidizing organisms were many times more common in the A horizon than in B_{ir} horizon. The implications are that dicarboxylic and tricarboxylic acids

are formed in the soil and act as complexing organic compounds with the metals.

The inference by McKenzie, et al. (ibid.) that a metal-organo complex is involved as a vehicle in the movement of iron in the profile serves to introduce another mechanism commonly described by soil scientists as being involved in podzolization. Kaurichev, et al. (1958) summarizes much of the Russian research on the formation of iron-organo complexes in the process of podzolization as follows:

> "1. In soils with temporary excess moisture, reducing processes appear during the spring that lead to the formation of ferrous iron.
>
> "2. The ferrous iron, reacting with water-soluble organic substances, forms complex organic iron compounds. Upon later oxidation of the iron these compounds maintain a high solubility and migrate through the soil.
>
> "3. There is a possibility of the formation of complex organic-iron compounds under conditions of the formation of podzolic and bog soils as well as soloths, solonetz and depression podzolized soil."

Bloomfield (1953, 1954) found that aqueous leachates of coniferous and broadleafed forest litter readily dissolved hydrated ferric and aluminum oxide with the subsequent formation of soluble ferrous and aluminum complex compounds. Such a mechanism would remove the necessity of first reducing the iron as is necessary in the scheme postulated by Kaurichev, et al. (ibid.). However, another mechanism or other mechanisms are necessitated for stopping the mobilized materials in the B horizon.

From the data presently available it appears that no single mechanism is totally responsible for sesquioxide transport in the process of podzolization. The reduction in the A horizons, movement and subsequent oxidation in the B horizon appears, from laboratory and field data, to be a very plausible mechanism. Complex metal and organic compounds have been shown to be a plausible solubilizing mechanism, both with complexes of the ferric and ferrous ions as well as with aluminum for their movement in the soil. Further field evidence now seems to be in order to establish this mechanism as a major contributor in the podzolization process.

Complex Formation and Chelation Reactions

Martell and Calvin (1952) have described a complex as being a substance with an electron donor that combines with the metal ion. However, if the substance which combines with the metal possesses two or more donor groups so that one or more rings are formed, a chelate compound or metal chelate is formed and the donor is said to be a chelating agent.

The authors represent schematically simple examples of complex formation and chelation reactions in the following manner, without further consideration of the nature of the bonds:

I - Metal Complex $M + 4\,A = A - \overset{\overset{A}{\uparrow}}{M} - A$ $\underset{\downarrow}{A}$

II - Metal Chelate $M + 2\ A\text{-}A = A - \overset{A}{\underset{A}{M}} - A$

Where: A-A represents a chelating agent
M represents a metal ion
A represents a complexing agent

This type of ring formation was termed chelation by Morgan and Drew (Martell and Calvin, 1952) and the term has been used to cover all types of ring systems with metal and with hydrogen, without regard to the nature of the chemical bond involved. However, as in ordinary complex compounds, the type of linkage which binds the metal into the chelate ring may be the ordinary covalent or the coordinate covalent type with some partial ionic character of these covalent bonds. Since many organic molecules have more than two positions through which covalent or coordinate covalent bonds with the metal may be formed, the terms unidentate, bidentate, tridentate, quadridentate, etc., were proposed by Morgan to denote complexes formed with molecules or ions containing one, two, three, four, etc., donor groups respectively. Obviously, complexes with unidentate substances would not involve chelation. Table 3 in the Methods section shows the chemical formulae and characteristics of some chelating agents used.

The factors contributing to the stability of a metal chelate are discussed by Lehman (1963). The author classifies such factors in three categories: (1) effect of metal ion, (2) effect of chelating agent, (3) effect of

environment. Based on the type of bonds formed, the size, charge, and the electro-negativity of the metal ion plays a role in the complex stability. A chelating agent exerts its influence through: the number of rings formed by a molecule of chelant and the metal ion; the size of the chelate ring; the donor atom, which determines the type of bond formed; resonance stabilization; steric effects and entropy effect. Among the environmental factors affecting the chelation equilibrium, temperature plays a role. Increasing temperature generally results in a decrease in stability constant. Since chelating agents are generally Lewis bases and will react with Lewis acids, pH should also be considered. Hydrogen ion will compete with metal ion for the chelant where the stability constant is low. However, the metal chelates with high stability constant are unaffected by low pH. Effective chelation at high pH's depends on the solubility product of the hydroxide or association constant of the hydroxide complex, i.e., solubility product of ferric hydroxide is 10^{-36} and at a pH of 8 or 9 it becomes difficult to get good chelation of iron with EDTA.

Soil Organic Matter and Chelation

Among the mechanisms responsible for the complexing of the metals by soil organic matter, chelation and complex coagulation, ion exchange, surface adsorption, and peptization reactions are described (Mortensen, 1963). Very little

is known concerning the nature of the ligands in polymeric components of organic matter which chelate metals, but carboxyl, carbonyl, hydroxyl, and amide groups are probably involved.

A general classification of soil organic matter is given by Allison, 1965, and Allison, et al., 1965. The organic matter is divided into the following categories: "(1) fresh plant and animal residue capable of rapid decomposition and loss of identity with simultaneous release of nutrients, (2) 'humus' which represents the vast bulk of resistant organic matter, having a high adsorptive capacity for cations and capable of improving soil structure, and (3) inert forms of nearly elemental C, such as charcoal, coal or graphite, which are occasionally present in appreciable quantities."

Broadbent (1953), while considering the constituents of plant tissue as precursors of soil organic matter, groups such constituents into more specific divisions as follows: (1) polysaccharides, (2) lignin, and (3) protein. More recent study (Mehta et al 1961) indicate that carbohydrates account for no more than 20% and polysaccharides less than 2% of the soil organic matter. Polysaccharides are also readily attacked and utilized by the soil organisms. Because of such susceptibility to microbial attack the principal structural polysaccharides of plants are therefore not likely

to accumulate in soil, whereas lignin is broken down only slowly. Nevertheless drastic alteration takes place in plant lignin during the course of decomposition in soil. Nitrogen accounts for 5% of the soil organic matter. Much of the organic nitrogen is in the form of polypeptides and amino acids intimately complexed with polysaccharides, lignin derivatives, and pigments (Bremner, 1965).

In addition to the intermediary products of organic matter breakdown and secondary synthetic products of microbial action, there exists in soil an accumulation of the more resistant products of decomposition: the soil humus. The native organic fraction of soils is made up of a heterogeneous mixture of polymerized aromatic molecules, polysaccharides, bound amino acids, uronic acid polymers, and various organic phosphorous compounds. By definition humus is a complex mixture of amorphous and colloidal substances arising from modified plant materials and synthesized microbial tissue. The characterization of humus is far from complete and concepts concerned with its formative processes are, to a large extent, speculative (Stevenson, 1965).

Mortensen and Himes (1965) recounted some difficulties associated with the fractionation and qualitative study of the soil organic matter. Some of these problems can be overcome. The most important is the removal of inorganic constituents such as clay, salts, and metals if the

physico-chemical properties of the organic compounds are to be studied. The authors have fully discussed the various procedures used for fractionation of organic matter extracts. Such procedures include partial fractionation of the components in organic matter extracts by precipitation with acid or metal salts or solubility differences in organic solvents, chromatographic separations of crude preparations, separation of substances by means of an electric current, diffusion and sedimentation.

Studies by several researchers have shown that most of the principal chelating donor groups are present in soil organic matter. Such groups include amino, imino, keto, hydroxy, thioether, carboxylate, and phosphonate groups. Many ligand groups probably function largely as centers for ionic exchange but chelation-type reaction no doubt occurs (Mcrtensen, 1963). Although the ligand groups in polymers are not free to move and cluster around a metal ion in a way small ligands behave, and moreover the number of chelate sites are comparatively small, a few ligand groups should be found in arrays which are sterically favorable for chelation. Side chain groups are usually more effective in binding metals than the terminal groups (Guard and Wilcox, 1956).

The study of Bloomfield in 1956 on the mobilization of iron in podzol soils by aqueous leaf extracts suggests that the polymeric components of organic matter chelate

metals. Bloomfield recognizes polyphenols as being the principal chelators in aqueous leaf extracts. Schnitzer (1954) and Schnitzer and DeLong (1955) have indicated the considerable chelating ability of polysaccharides in aqueous leaf extracts. These compounds are also found to be a constituent part of fulvic acid. The presence of amino acids in hydrolyzates of soil organic matter and the chelating ability of proteins as well as a number of low molecular weight compounds has been confirmed by a number of investigators (Mortensen, 1963). All such studies suggest the chelation reaction as one of the mechanisms by which organic matter forms complexes in soil. However, in a more specific study Schnitzer and Skinner (1963) investigated the reactions between a number of metal ions and the organic matter of a podzol Bh horizon. Using potentiometric and conductometric titration, adsorption and infrared spectroscopy and flocculation methods, they concluded that the organic matter formed stable water soluble complexes with all of the metals studied (Fe^{+++}, Al^{+++}, Ca^{++}, Mg^{++}, Cu^{++}, and Ni^{++}) over the pH range encountered in podzol soils. Ferric iron, aluminum and copper formed water soluble 1:1 molar complexes at pH 5. However, a range of molar complexes varying from 1:1 to 6:1 were formed and the complexes were increasingly rendered water insoluble as more metal was complexed. The number-average molecular weight of organic matter used in this

study in two different solvents was found to be 670, and from the molecular weight and from ultimate and functional group analysis, the molecular formula calculated to be $C_{21}H_{12}(COOH)_6(OH)_5(CO)_2$.

The same authors (Schnitzer and Skinner, 1963), in a subsequent study of the reactions between different forms of iron and aluminum and the organic matter of the podzol Bh horizon, showed that on continuous wetting and leaching in a period of one week one mole of organic matter mobilized one mole of iron from goethite and an iron saturated exchange resin, and 1.1 mole of aluminum from aluminum saturated exchange resin. The metal uptake in reaction with goethite and gibbsite was decreased with an increase in pH. The methylation of most of the active acid groups reduced iron uptake indicating the important role of carboxyl groups in the organo-metallic reactions.

Schnitzer and Skinner (1966) carried on a study of the stability constant of Cu^{++}, Fe^{++}, and Zn^{++} fulvic acid complexes. The results obtained show that the log K values for Cu-fulvic acid complexes were pH dependent, that is, these values were increased from 5.78 to 8.69 as pH was increased from 3.5 to 5. A slight increase was observed for Zn-fulvic acid complexes while the Fe^{++}-fulvic acid complexes were unaffected. The order of stabilities of complexes formed between fulvic acid and Cu^{++}, Zn^{++}, and Fe^{++} did not

follow the Irving-Williams series but was instead $Cu^{++} > Fe^{++} > Zn^{++}$. In a later attempt to evaluate the methods for the determination of stability constants of metal-fulvic acid complexes, Schnitzer and Hansen (1970) found the following order of stabilities at low pH:

$$Fe^{+++} > Al^{+++} > Cu^{++} > Ni^{++} > Co^{++} > Pb^{++} = Zn^{++} > Mn^{++} > Mg^{++}$$

An increase in ionic strength (u) at a pH as low as 3 caused a linear decrease in log K values (stability constants). This was especially true for Co^{++}-fulvic acid complexes. The authors believe that stability constants measured at low (u) are more relevant to soils than those determined at higher (u).

Schnitzer and Desjardins (1969) studied the natural leachate from a humid podzol and analyzed it by chemical and spectroscopic methods. About 87% of the dry, ash-free weight of the leachate was found to be fulvic acid, the remainder consisting mainly of polysaccharides and nitrogenous compounds. The organic matter in the leachate had all the characteristics of an efficient metal-complexing agent, as evidenced from its high water solubility, thus playing a significant role in metal organic matter interactions in soils.

Extraction of Organic Matter from Soils

Mortensen and Himes (1965) have reviewed the extraction procedures of soil organic matter as follows: (1) proximate analysis, (2) adsorption of organic matter on clay, (3) organo-mineral gels, (4) aqueous extractants and chelating extractants.

The proximate analysis involves attraction between solute and solvent and gives some general information on the quantity of different classes of compounds. In addition to differential solubility problems, adsorption of organic matter on the surface of soil minerals, particularly clay minerals, make the extraction of organic matter difficult. Some organic molecules are apparently held to the clay surface through C-H...O (clay-mineral surface) bonds, although any sorbate capable of supplying electrons to the incomplete P orbitals of adsorbed or lattice aluminum could be adsorbed.

Compounds containing electro-negative elements may be adsorbed by a hydrogen bonding mechanism. Negatively charged organic anions and polyanions are apparently linked to the clay surface through polyvalent inorganic cations and ionized carboxyl groups (clay-M-OOCR). Among those cations adsorbed, aluminum or iron hydroxide polymers can be mentioned. It appears that the reagents which decompose the clay lattice, such as phosphate, fluoride, strong base and hydrofluoric acid may be most useful for organic matter extraction.

Organo-mineral colloids in the soil, particularly those occurring as a result of interaction of organic matter with aluminum and iron, can be transferred into water-soluble hydroxy complexes in a slightly alkaline medium, while a strongly alkaline medium may completely hydrolyze them.

The presence of free monomeric forms of organic molecules such as amino acids and hydrocarbons necessitates their removal in order to increase the efficiency of extraction. Such pretreatment procedures include the use of organic reagents such as benzene, methanol, chloroform, and ethanol, as well as ball-milling the soil and sulfacetolysis or densimetric fractionation to remove the "unhumified" or unadsorbed material. Hydrofluoric acid-hydrochloric acid mixtures and decalcification with 0.1N hydrochloric acid have in some instances increased the efficiency of extraction (Mortensen and Himes, 1965).

Aqueous inorganic and organic extractants have been widely used to extract soil organic matter. The successful use of natural and synthetic chelating agents to extract metals and organic matter from soil are to some degree indicative of the circumstantial evidence that metals are chelated by organic matter.

Several researchers have used chelating agents to desorb the micronutrients from the soil and make them available to plants. Dion and Mann (1946) have shown that neutral

sodium and potassium pyrophosphates, as extractants for manganese, are much more effective than the corresponding orthophosphates and that a soluble complex of mangani-pyrophosphoric acid $H(MnP_2O_7)$ has been identified in the buffered pyrophosphate in which manganese has a valence of 3. Heintz and Mann (1947) indicate that various organic hydroxy-acids are almost as effective as pyrophosphate and more effective than the corresponding unsubstituted acids as soil manganese extractants. Kanwar (1954) was able to correct the copper deficiency caused by fixation by paddy soils high in organic matter content. Sodium versenate and sodium pyrophosphate appeared to be satisfactory complex forming agents. Misra and Sharma's (1961) experimental results reveal that the Cu^{++} ions are adsorbed from copper sulphate solution by soils and compost alike, but the adsorption greatly depends upon $CaCO_3$ content and pH of the material and that the adsorbed Cu^{++} is readily extracted by organic acids.

Experiments using the soluble component of plant residues as well as animal byproducts as extractants of trace elements have been conducted by several scientists. Hurwitz (1949) has demonstrated the ability of soluble components of alfalfa meal and oat straw to increase the amount of copper leached from a sandy loam and silty clay loam soil. He also indicates that the amount of copper leached from the soil is directly proportional to the amount of plant residue used.

Furthermore, he concludes that the copper which exists in metalo-organic complex is the form affected by the soluble components of the plant residue.

Miller and Ohlrogge (1958), in a study of influence of chelate-containing materials on the availability of trace metals to plants, have observed a reduction in absorption of Zn and Fe by plants upon addition of water-extracts of barnyard manure to nutrient solutions. They also noticed that such extracts decreased the availability of Zn and Cu when it was applied to the soil. It was concluded that the chelating agents held the micronutrients in a less available form.

Matomura (1961) recognized that the extracts from milk vetch had a fairly high dissolution capacity for both insoluble inorganic iron compounds and iron in soil. The dissolved iron was mainly in ferric forms and only 20-40% of the total dissolved iron was in ferrous form. He also noticed that the dissolving capacity for aluminum was much less than for iron. Furthermore, he concluded that fatty acids and complex chelating materials in extracts were responsible for dissolution of iron and reduction of dissolved ferric iron was due to some reducing substances which were formed during the fermentation process.

The results of studies by a number of researchers have revealed that the illuvial organic matter in the B horizon of podzolic soils is easier to extract than the organic

matter in the surface soil. Such data also suggest the possibility of the precipitation or flocculation of organic matter by iron and aluminum in these soils, and that complexing these metals renders the organic matter soluble in water. A variety of natural and synthetic organic chelating agents as well as inorganic reagents have been used to extract both the organic matter from the surface and subsurface layers of podzolic soils.

An extensive review concerning the solubilizing effect of naturally occurring compounds, such as material synthesized by plant cells, e.g., ADP, as well as other natural salts of organic and inorganic acids on the insoluble matter in nature, can be found in articles by Mandle, Grauer, and Neuberg (1952 and 1953). The authors consider a number of such naturally occurring compounds as being "obligatory intermediates, continually reformed, or final products of metabolism, or cellular constituents."

Synthetic organic chelating agents have been used to extract metals complexed by soil organic matter with a subsequent dispersion of soil organic matter. Martin and Reeves (1957) have used a number of organic chelating agents in dealing with podzolic illuvial horizons. Their experimental results reveal that acetylacetone appears to be the most satisfactory reagent and readily forms complexes with transitional metals. The chelates of Al and Fe with acetylacetone are

extremely stable with overall formation constants (or log $k_1k_2k_3$) of 22.3 and 26.2 respectively. Cupferron, another organic reagent they used in their study, was not satisfactory as an extractant. Neither was the oxine, which proved to be a slow extractor. They concluded that even if true metal coordination complexes exist in these soils, extraction of organic matter would be governed by other factors such as pH and the nature of the cation associated with the reagent.

In a subsequent study Martin and Reeves (1957) report on the effect of the concentration of aqueous acetylacetone as well as the effect of extraction time and pH on the extraction of organic carbon and sesquioxides. Their data clearly show that reaction time has little influence on extraction of carbon, while increasing reagent concentration causes an increase in carbon dispersion. Also, 0.2M acetylacetone at pH 7 removes more carbon and in some cases more Al complexes than at pH 4.2, but less Fe is extracted at higher pH. Furthermore, the superiority of pyrophosphate over acetylacetone was confirmed. While it is difficult to explain these findings in terms of chelate stability (over-all stability, log constants of Cu-pyrophosphate and Cu-acetylacetone are 10.1 and 17.4 respectively), the authors suggest that the real explanation may lie in the fact that the acetylacetone at pH 7 contains only 1-2% free anion and the Na^+ concentration is low. Thus metals removed from the organic matter are

replaced predominantly by H^+. With $Na_2H_2P_2O_7$, the degree of ionization is large and a larger fraction of the active groups on the organic matter surface is occupied by Na, resulting in greater dispersion.

Other organic complexing reagents such as 8-hydroxyquinoline, disodium dihydrogen ethylenediaminetetraacetic acid, cupferron, acetylacetone, as well as the inorganic chelating agent Na-pyrophosphate, were used to extract organic matter from soil by Choudhri and Stevenson (1957). They studied the effects of pretreatment and exchangeable bases, removal of free iron and aluminum oxides, and finally, removal of silicate minerals on the organic matter extraction. They concluded that the removal of calcium and free iron and aluminum oxides increased the solubility of organic matter by almost all the reagents they used, but had no effect on extraction by pyrophosphate. However, the removal of silicate minerals was effective in facilitating the extraction of humic acid by pyrophosphate as well as other chelating agents used in the study.

Parson and Tinsley (1960) have used formic acid, a polar compound, as an extractant for soil organic matter, particularly polysaccharides. They state that one of the advantages of the solvent is the lack of either oxidizing or hydrolytic properties in the anhydrous condition. They also noted an increase in extraction efficiency upon addition of inorganic cations to the extractant.

Inorganic reagents have been widely used to extract soil organic matter with some success. Bremner, et al., (1946) have used pyrophosphate, orthophosphate, and some sodium salts of organic compounds such as citrate and oxalate as extractants of organic matter. They noticed that upon dialysis of the pyrophosphate extract the water-soluble organic nitrogen is not removed while most of the metals are removed. Their results further indicate that, on the whole, the compounds that are good polyvalent cation extractants are also good organic matter extractants. They infer that part of the polyvalent metals is combined as co-ordination complexes with part of the organic matter, and the presence of the metals renders organic matter in the complexes insoluble in water. They also indicate that the extracting power of 2% Na-hydroxide is primarily due to degradation of the high molecular weight compounds initially present in the soil.

Bremner and Lees (1949) further investigated the question whether the solubility of organic matter is governed by the nature of the association between organic matter and metals, as well as the ability of the anion of the extractant to remove the interfering metals as either insoluble precipitates or soluble coordination complexes. Among the accompanying cations used in the extractants, Na^+, K^+, and NH_4^+ gave rise to an efficient extraction, while Ca proved to

be a chief interferant in organic matter extraction. In the above studies organic nitrogen was taken as an index for soil organic matter. However, in a subsequent study, Bremner (1949) found that the organic carbon and nitrogen are intimately associated so that the organic carbon is dissolved only in proportion to organic nitrogen.

Dilute inorganic acids have been used to extract organic matter from the podzolic soils by Schnitzer and Wright (1957). Two per cent of the carbon of the Ao horizon and as high as 96% of the carbon of a B horizon of a podzol soil were extracted by HF, HCl, and a mixture of HCl-HF. An acid concentration higher than 0.5% was less effective. The amount of carbon extracted by 0.5% HCl showed a correlation with extracted Fe and Al, with maxima occurring in the B horizon extracts.

In a later study by Schnitzer, et al., (1958), a survey of the extractive power of fifteen inorganic reagents was made. Included among them were NaOH, $Na_4P_2O_7$, Na_3PO_4, NaF, and NaCl. The only organic reagent used was Na_2-EDTA. The pH ranged from 1.4 to 13.1, and the amount of organic matter extracted varied with horizon as well as with the extractant. They concluded that while only NaOH removed appreciable amounts or organic matter from the Ao horizon, others such as $Na_4P_2O_7$, Na_3PO_4, NaF, Na_2CO_3, and EDTA, extracted more than 80% of the organic matter in the B_{21} horizon.

Evans (1959) noted that the extent of organic matter extraction tended to rise with the pH of the extracting solution. The chelating reagents extracted more organic matter than other extractants of comparable pH, but extracts by all reagents rose with increasing time and temperature. Tinsley and Salam (1961) also confirmed the suitability of Na-pyrophosphate as well as citrate, oxalate, and sulphate at comparable concentration and pH values for organic matter extraction. The role of pH was also studied by the above authors and it was in agreement with Evan's previously mentioned studies.

It has been demonstrated that secondary Fe and Al compounds and organic matter in soil reflect processes of soil formation and influence soil structure and plant nutrient status. Fe and Al exist in different forms in soil, particularly in crystalline oxides and silicates, amorphous hydrous oxides, and as complexes with organic matter. The form in which they appear is a diagnostic feature of the B horizon of podzols and of importance in identification of the podzolic soils. A collective term of "active" material has been assigned to the colloidal humus and sesquioxides complexes indicative of high cation exchange capacity and physico-chemical properties. Therefore many researches have been conducted to design a simple extraction technique to separate the active from inactive compounds and complexes

with the object of improving the identification and classification of podzols.

For some time free Fe oxides have been extracted from soils by dithionite-citrate-bicarbonate extracting solution (Mehra and Jackson, 1960). McKeague and Day (1966) made a comparison of the extractability of iron and aluminum with dithionite and acid ammonium oxalate, using some Canadian podzolic soils. Their results reveal that the oxalate extraction dissolved much of the iron and aluminum from the amorphous materials, including the amorphous hydrous oxides of recent weathering as well as metal-organo complexes, but very little from crystalline oxides. On the other hand, the dithionite extraction dissolved a large proportion of crystalline iron oxides, as well as much of the amorphous materials. They also noticed that oxalate-extractable Al frequently exceeded dithionite-extractable Al, and the ratio of oxalate to dithionite-extractable Fe commonly was high for B horizons. They concluded that since oxalate extracts iron and Al organic complexes from soil, some of the Fe and Al extracted by oxalate from B horizons of podzols existed as metal-organic complexes.

Franzmeier, et al., (1965), used a mixture of pyrophosphate and dithionite in solution at pH 7.3 to extract Fe, Al, and organic C from podzol B horizons. However, dithionite dissolves Fe silicate minerals and amorphous Fe oxides.

Titova (1962) has shown that neutral sodium pyrophosphate is capable of extracting iron from hydroxide as well as iron containing minerals. Further data by Kononova, et al.(1964), indicates that the neutral sodium pyrophosphate is rather a strong reagent which decomposes minerals and frees the iron and aluminum. Therefore, the above authors do not confirm the hypothesis that the pyrophosphate solution extracts only the Fe and Al fixed by organic substances.

McKeague (1967) compared Franzmeier's extracting solution, 0.1M Na-pyrophosphate and 0.2M acidified ammonium oxalate as extractants of the accumulation products in podzols. His data suggest that o.1M Na-pyrophosphate solution extracted some of the Fe-, Al-organic matter products in podzol B, but did not dissolve the inorganic amorphous or crystalline Fe and Al substances tested. The oxalate solution extracted Fe and Al from amorphous inorganic substances as well as amorphous Fe- and Al-organic matter complexes. It did not dissolve crystalline Fe oxides. The pyrophosphate-dithionite solution extracted a large proportion of Fe and Al from crystalline oxides as well as amorphous organic and inorganic forms. He recommends either acid ammonium oxalate or 0.1M pyrophosphate as useful extractants for estimating the accumulation products in podzol-like B horizons.

Bascomb (1968) extracted Fe and carbon from a number of British soils using 0.1M K-pyrophosphate solution.

Studying the effect of pH of solution on extraction of Fe, he used a series of Fe-containing materials including a freshly precipitated hydrated $Fe(OH)_3$, a poorly crystalized lepidocrocite, and x-ray amorphous Fe-oxide, a moderately crystalized goethite, and a tropical laterite. He observed that the extraction of crystalline oxides was slight at pH 10, compared with pH 7. He also suggests little attack on silicates by pyrophosphate. In conclusion he states that pyrophosphate extracts peptizable organic matter and separates amorphous forms from the less active crystalline Fe oxides better at a pH of 10 than at a pH of 7 or 13.

MATERIALS AND METHODS

Soils Used in the Study

The soil profiles studied in this research consist of two groups of profiles: (1) Spodosols developed on a sandy Topo-biosequence in Northern Michigan and (2) well-drained Spodosols with varying degree of spodic horizon development. (The author expresses his appreciation to Dr. J. B. Collins and Dr. D. A. Lietzke for their permission to use these soil samples in this study.) In addition to spodic horizons from the above profiles, some other horizons such as A_1, A_2, argillic horizons and fragipans were also included in the study. Some of the physical and chemical properties of the soils relevant to this study as well as the kinds of horizons used in the study are given in Table 1, and the approximate locations of the sites are shown in Figure 1. The legal descriptions of the locations of the profiles studied are also given in Table 2. The full profile description of the soils are given by the above authors in their respective studies. However, a short description of each profile will be given in the succeeding paragraphs.

The first group of profiles were selected from a Topo-biosequence so that it reflects a gradation in soil moisture

regime and its relationship with the vegetation along the slope (Collins, 1971). The soil parent materials are extensive areas of sandy and gravelly tills and outwash plains of late pleistocene age. These plains are pitted with glacial kettle holes. The upland area is known as a "Jack pine area" of Michigan. Various types of bog and marsh vegetation have developed in the adjoining kettle holes. The dominant shrub cover is known to be of the type of "leather leaf" being adapted to the poorly-drained acid bog. The soil types can be briefly described as follows:

Kinross sand is a poorly drained, Histic Haplaquod (low-Humic-Gley) which is developed from medium to very strongly acid sand and gravel tills of late pleistocene age. This soil has an organic surface which is thirteen inches thick. The spodic B horizons contain aggregates which are apparently held together by the reddish-brown humus-sesquioxides and some clay. Kinross series, which includes former Low-Humic-Gley soils, are the poorly to very poorly drained member of catenas which includes the well drained Grayling or Rubicon soils, the moderately well drained Croswell, and the somewhat poorly drained AuGres soils.

Saugatuck-AuGres sand is a somewhat poorly drained pedon in the Saugatuck series but borderline to AuGres. It ranges from Aeric Haplaquods to Entic Haplaquods in characteristics (Ground-Water-Podzols). This soil is developed in

Table 1. Some physical and chemical properties of the profiles studied

Soil series and horizons		Lab No.	Parent material	Natural drainage	Depth (inches)	Munsell notation	pH	% clay	CEC NaOAC (pH 8.2) m.e./100 gm
Kinross	$B_{21}h$	1	sand & gravel drifts	poorly drained	11-21	5YR 3/3	4.5	2.1	8.2
	$B_{22}hir$	2			21-27	5YR 4/3	4.7	1.8	6.1
Saugatuck-AuGres	$B_{21}hir$	3	sand	somewhat poorly drained	3- 7	5YR 3/3	4.8	8.8	17.3
	$B_{22}hir$	4			7-11	5YR 3/3	4.8	6.7	14.1
	$IIB_{21}hir'$	5			16-23	5YR 3/4	4.9	3.1	14.3
	IIBhir'm	6			23-33	5YR 3/2-3/3	5.0	1.1	6.9
AuGres-Croswell	$B_{21}hir$	7	medium & coarse sand	somewhat poorly to moderately well drained	13-14	5YR 4/6	4.7	4.3	7.5
	$B_{22}hir$	8			14-21	10YR 4/4	4.7	4.6	4.7
Croswell-Graycalm	$UPPE_{21}hir$	9	sand to loamy sand & sand drifts	moderately well to well drained	3- 5	5YR3/3 to 7.5YR4/4	4.9	5.0	4.9
	$lowB_{21}hir$	10			5- 7	5YR3/3 to 7.5YR4/4	5.1	3.6	4.2
	$B_{22}hir$	11			7-15	7.5YR4/4 to 7.5YR5/4	5.4	2.9	3.1
Omega	B_{22}	12	sand	well drained	7-12	7.5YR 4/4	6.0	2.8	5.3
Eastport	B_{21}	13	sand	well drained	13-17	7.5YR 4/4	7.2	1.3	2.5
Rubicon	A_1	14	sand	well drained	0-2 1/2	10YR 2/1	4.5	4.9	11.4
	$B_{21}ir$	15			4-6	5YR3/4-4/4	4.5	3.7	17.9
	$B_{22}ir$	16			9-14	7.5YR 4/4	5.5	2.1	3.2
	ortstein	17			9-27	7.5YR 4/4 to 5YR3/2	5.0	0.9	3.9
Hiawatha	A_1	18	sand	well drained	0-2	5YR 2/1	5.5	4.1	17.7
	A_2	19			2-5	5YR5/1-4/1	5.5	2.2	4.2
	$B_{21}hir$	20			5-11	5YR 2/2	4.5	6.5	16.2
	$B_{22}ir$	21			11-17	5YR 3/4	5.5	2.3	12.5
Onaway	A_2	22	loam or sandy loam glacial till	well drained	6-6	5YR 5/3	4.5	4.3	3.4
	$B_{21}ir$	23			6-9	5YR 3/4	5.0	15.8	16.5
	$B_{22}ir$	24			9-12	5YR 5/6	5.0	13.7	11.4
	$B_{22}t$	25			24-28	5YR 4/3	7.0	24.9	17.1
Munising	A_1	26	sandy loam glacial till	well drained	0-1	5YR 2/2	5.0	3.8	26.5
	A_2	27			1-9	5YR 6/2	4.5	.38	7.5
	$B_{21}hir$	28			9-13	5YR 3/3-3/2	4.5	10.6	25.9
	$B_{22}ir$	29			13-21		5.0	7.8	14.8
	B_3X	30			21-29	2.5YR 4/4	5.5	4.4	3.5

Table 2. Soil type names and legal descriptions of locations of the profiles studied (see also Fig. 1)

Soil type	Location
Omega fine sand	SW 1/4 of SE 1/4, Section 27, T 46 N, R 25 W. Marquette County
Eastport sand	SW 1/4 of SW 1/4 of SE 1/4 of NE 1/4, Section 9, t 7 N, R 17 E. St. Clair County
Rubicon sand	NE 1/4 of NE 1/4, Section 1, T 45 N, R 19 W. Alger County
Hiawatha sand	NW 1/4 of SE 1/4, Section 7, T 53 N, R 35 W. Houghton County
Onaway fine sandy loam	SW 1/4 of SW 1/4, Section 33, T 40 N, R 24 W. Delta County
Munising loamy sand	SW 1/4 of NE 1/4, Section 4, T 51 N, R 31 W. Baraga County

Kinross,Saugatuck-AuGres, AuGres-Croswell and Croswell-Graycalm are from a sandy topo-biosequence which is located in the Northern part of Michigan's lower peninsula on State Forest land, in South Central Crowford County.

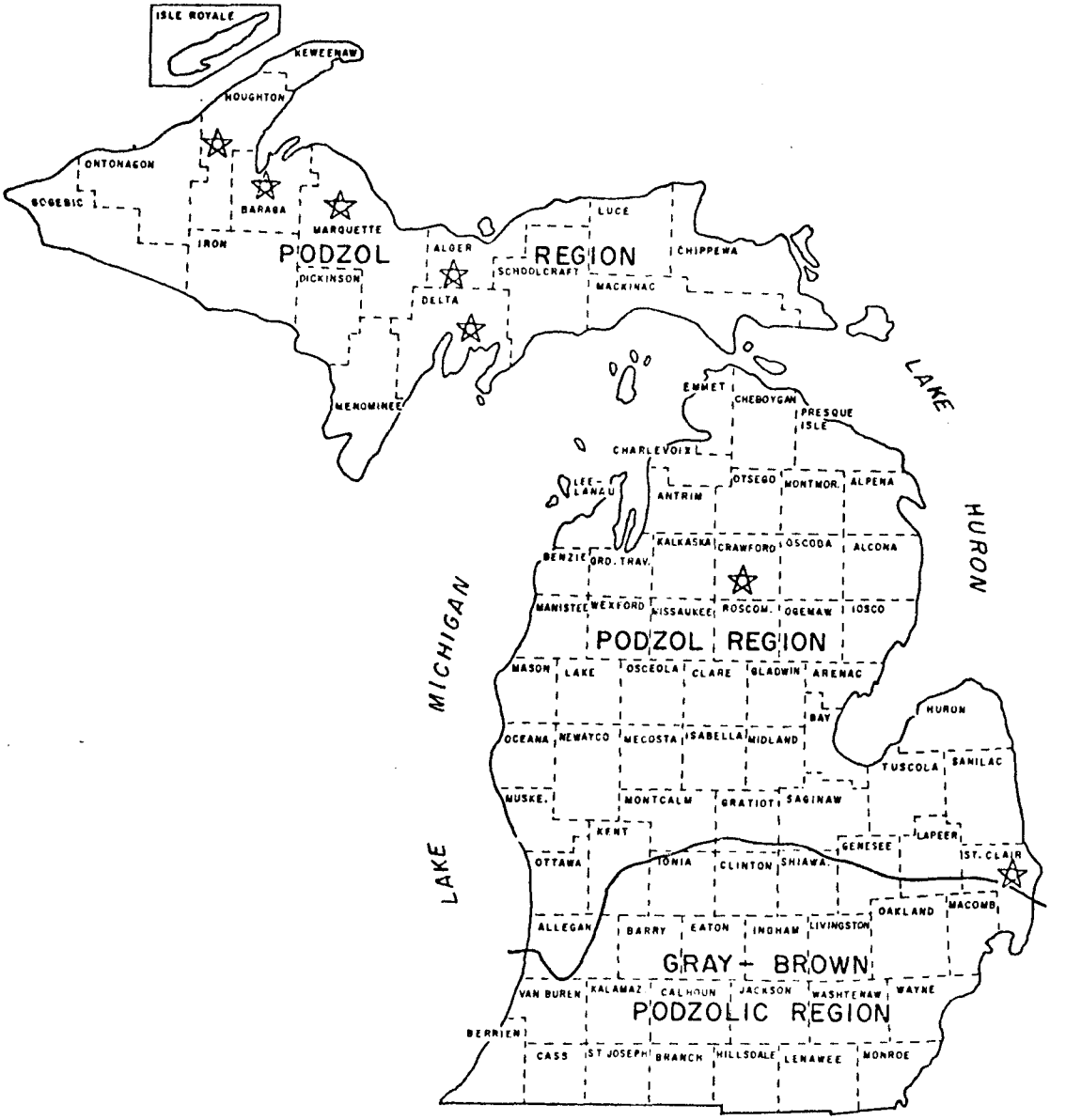


Figure 1. Map of Michigan showing locations of representative soils used in the study

sandy deposits of late pleistocene age. This soil has a strongly cemented ortstein in the lower B horizon with well-coated sand grains in the spodic horizons. The water table varies during the growing season and averages 20" below the surface. Saugatuck soils are imperfectly to poorly drained Ground-Water-Podzols of a catena which includes imperfectly drained AuGres and Arenac soils without a cemented B horizon, the poorly drained Roscommon soils (which are less acid than the Kinross soils), the well drained Rubicon, and the moderately well drained Croswell soils.

AuGres-Croswell sand is an imperfect to moderately well drained pedon in the AuGres series but borderline to Croswell. The water table averages 36" deep during the growing season. This soil has characteristics which range from Entic Haplaquods to Entic Haplorthods and is developed in medium and coarse sand. It is a borderline case of AuGres with respect to drainage and spodic horizon development.

Croswell-Graycalm sand is a moderately well to well drained pedon in the Croswell series but borderline to Graycalm. It is classified as Entic Haplorthods (Gray Brown Podzol intergrade). It is developed from a range of parent material extending from medium and coarse sands to loamy sand and sand drifts with thin textural bands in the lower part of the profile. A weak fragipan occurs at the depth

of 23-28". Its B_2 horizons have characteristics of a weakly developed spodic horizon. The water table averages 58" during the growing season.

The second group of profiles are developed from sandy to coarse loamy materials with well-drained moisture regimes. Such profiles were selected on the basis of increasing intensity of pedogenic processes as evident in the amount of illuvial organic carbon, Fe, and Al in the spodic horizon (Lietzke, 1969). There are two groups of soils included in these well drained Spodosols, those also having textural B horizons and those without textural B horizons. These soils include a range of spodic horizon development from the weakest to the strongest development and are listed in Table 1, and described briefly below.

Omega fine sand is a well drained Typic Udipsamment (Brown Podzolic soil) which has developed from sand in an outwash plain. The vegetation is jack pine, sweet fern, reindeer moss, and blueberries. Some of the Omega series is found to have intermittent thin gray A_2 and dark reddish-brown B_2 horizons suggesting a weak podzol profile. However, they generally lack evidence of spodic horizon development. Omega is a well drained member of a catena which includes the somewhat poorly drained AuGres and the poorly drained Roscommon series.

Eastport sand is a well drained Spodic Udipsamment (Regosol-Podzol intergrade) which has developed from sand on lake benches and beach ridges. The vegetation is aspen and choke cherry, with ground cover of weeds and grasses. A few pedons of this series are known to have weakly cemented thin chunks of ortstein in the lower part of the B horizon. The well drained Eastport, along with the somewhat poorly drained Roscommon, form a drainage sequence or catena.

Rubicon sand is a well drained Entic Haplorthod (weakly developed Podzol) which has developed from sandy parent material on outwash plains, till plains or moraines. The vegetation associated with this soil consists of red pine, oak, a few aspen, and ground cover of primarily bracken fern. The spodic horizons can be recognized in the field, and in some pedons a few weakly cemented chunks may be present in the B_{21}ir horizon. It is the well drained member of a drainage sequence that includes the moderately well drained Croswell series, the somewhat poorly drained AuGres series, and the poorly drained Roscommon or Kinross series.

Hiawatha sand is a well drained Typic Haplorthod (well-developed Podzol) developed in sand of outwash plains or glacial till. The vegetative cover at this site consists of cut-over hard maple forest with a quack grass and timothy sod. Hiawatha soils have strong and distinct spodic horizon development. In some pedons the B_{21}hir and B_{22}ir horizons

are slightly to strongly coherent in places, with fairly thick pieces of cemented ortstein which crush under moderate pressure. Hiawatha is the well drained member of the drainage sequence which includes the imperfectly drained Watersmeet (tentative series), Saugatuck (Ground-Water Podzol with cemented B), and the poorly drained Roscommon or Kinross soils.

Onaway fine sandy loam is a well drained Alfic Haplorthod (minimal Podzol grading to Gray Brown Podzolic) developed on calcareous loam or sandy loam glacial till in till plains or on moraines. The vegetation is mainly red maple, white birch, balsam fir and aspen. Onaway soils have a fine sandy loam upper sequence of horizons of black O_2 horizon, brown A_2 horizons, and a dark reddish-brown and reddish-brown B_2ir horizons of slight organic matter and iron accumulations, and a lower sequence of horizons of light reddish-brown and dark reddish-brown loam A_2' and B_{21}'t horizons, and a light brown and brown C horizons of loamy calcareous till. Onaway soil is a well drained member of the drainage sequence which includes somewhat poorly drained Mackinac and the poorly drained Angelica soils.

Munising loamy sand is a well drained Alfic Fragiorthod (Podzol grading to Gray Brown Podzolic soil with fragipan). This soil is developed in sandy loam glacial till in a morainic area of Wisconsin age. Hard maple and yellow birch

are the dominant vegetation in this location. The Munising soils are bi-sequal soils. Typically they have an upper sequum comprised of thin, black, fine sandy loam A_1 horizon, a pinkish gray loamy sand A_2 horizon, and dark reddish-brown and reddish-brown sandy loam Bir horizons. The lower sequum is comprised of a very compact fragipan of gray loamy sand A'_{2x} horizon, reddish-brown sandy loam B'_{21tx} horizon, reddish-brown sandy loam B'_{22t} horizon, and reddish-brown sandy loam C horizon. Munising is a well drained member of a drainage sequence which includes somewhat poorly drained Skanee soils and poorly drained Gay soils.

Methods Used in this Study

Methods used in this study consist of two parts: (1) the extraction procedures and (2) the quantitative determination of the illuvial organic carbon, Fe and Al in the soil extracts.

The aqueous extractants used in the study are of the type which have the ability to chelate metals. Such chelating agents include the tetra-sodium salt of pyrophosphoric acid (Na_4-pyrophosphate), an inorganic chelating agent, as well as the following Na salts of organic chelating agents: diethylenetriaminepentaacetic acid, pentasodium salt (Na_5-DPTA); ethylenediamine tetraacetic acid, disodium salt (Na_2-EDTA); and nitrilotriacetic acid disodium salt (Na_2-NTA).

The chemical formulae and the stability constants of these chelating agents with Fe and Al are presented in Table 3.

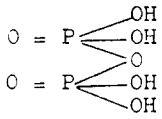
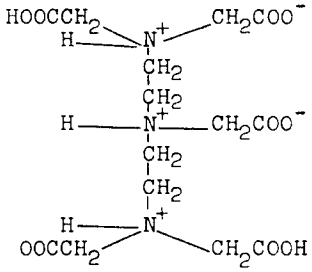
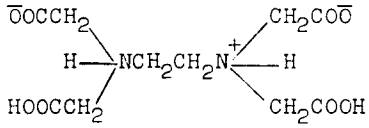
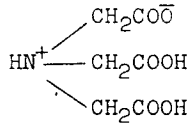
Extracting procedure: Bascomb's (1968) procedure was used, as follows: 2g. air-dry soil ($<$ 2mm) were placed in 250ml. centrifuge bottles (polypropylene) and 200ml of 0.1M extracting solution were added to the soils. The bottles containing soils and solutions were capped and shaken overnight at room temperature. Five drops of 0.4% superfloc were added and the bottles shaken again for five minutes. After this the samples were centrifuged at 2,000 rpm for ten minutes or until the supernatant liquid was clear in reflected light. The soil extracts were then transferred to plastic containers for further analysis.

Soil extract color: The soil extracts were placed in 100ml glass bottles, thus keeping the solution thickness uniform. The color values were determined in reflected light by means of a Munsell color chart.

Soil extract reaction: The hydrogen ion activity of the extracting solutions were determined before extraction and immediately after extraction. A glass electrode Beckman Zeromatic pH meter was used in the soil extract reaction measurement.

Fe and Al in the soil extracts: The extracts were analyzed for iron and aluminum using a 303 model Perkin-Elmer atomic absorption spectro-photometer. Acetylene and air were

Table 3. Chemical formulae and some of the equilibrium constants of the chelating agents used in this study

Ligand	Abbreviated formula	Metal ion	Equilibrium constants Log (K)
Pyrophosphoric acid 	($Na_4P_2O_7$)	Fe (II) Fe (III) Al (III)	
Diethylenetriamine-pentaacetic acid DPTA 	(Na_5DPTA)	Fe (II) Fe (III) Al (III)	16.5 28.6 -
Ethylene diamine-tetraacetic acid, EDTA 	(Na_2H_2EDTA)	Fe (II) Fe (III) Al (III)	14.33 25.1 16.3
Nitrilotri-acetic acid, NTA 	(Na_2HNTA)	Fe (II) Fe (III) Al (III)	8.82 15.9 -

used for iron determination as fuel and oxidant, respectively. The oxidant used for Al determination was nitrous oxide to provide a hotter flame. The percent Fe and Al in the extract were calculated using the following equation:

$$\% \text{ element} = \frac{CV(d.f.)}{(W)10{,}000}$$

Where V = volume in undiluted sample
d.f. = dilution factor
W = weight of sample
C = concentration of element in sample solutions obtained from standard curve in ppm

The elemental Fe and Al are expressed in percentage of the soil sample, oven dry.

Total carbon in soils before extraction: Total carbon in soils were determined by the dry combustion method using a "LECO 70 Second Carbon Analyzer". Soil samples were ground for six minutes in a high speed impact shaker, then one hundred milligrams of finely ground soil (80 mesh) was placed into a special ceramic crucible and one scoop (approximately 1 gram) each of iron chip and tin accelerators were added. The crucible was placed in the space provided in the combustion tube of the induction furnace through which O_2 was being passed. The combustion tube provides a temperature over 1670°C, sufficiently high to oxidize or burn the sample readily. The C in the sample was oxidized to CO_2. The gas mixture leaving the induction furnace was passed through a

dust trap to filter out the solid tin and iron oxides, followed by a sulfur trap containing MnO_2 to absorb sulfur gases which might have been oxidized during the combustion of the sample, and finally through a heated catalyst to oxidize any CO formed to CO_2. The moisture of the gas mixture was removed before it entered the analyzer by an anhydrone trap.

The gas mixture (O_2 and CO_2) which had undergone the combustion and purification processes was then passed into a cylinder located in a temperature-controlled oven ($450^{\circ}C$) in the analyzer. The thermal conductivity of the gas mixture in the cylinder was measured by means of a thermal conductivity cell of a thermistor-type. The output of the thermal conductivity cell was read on a special DC digital voltmeter as per cent carbon (%C).

Total carbon in soils after extraction: The soil samples (after being subjected to extraction) were washed with distilled water in #42 filter papers on glass funnels. The washings were repeated until the filtrate resumed a neutral pH. Six to nine hundred ml. of distilled water was used. The samples were then air-dried and their total carbons were determined by the dry combustion procedure already described.

RESULTS AND DISCUSSION

Preliminary Studies

Preliminary studies concerning the various factors affecting the extraction of Fe, Al, and carbon were conducted. The discussion of the results of such experiments follows:

Effect of concentration of the extractant: Solutions of 0.1M, 0.2M, and 0.5M Na_2-NTA and also 0.1M and 0.2M Na_2-EDTA were applied to soil samples. The extraction procedure of Bascomb was followed and slightly modified by using different concentrations of the reagents as indicated. The results are shown in Table 4. The selected spodic horizons as well as ortstein and fragipan samples do not seem to have released higher amounts of sesquioxide with increasing concentration of the reagent. However, the argillic horizon ($B'_{22}t$) of the Onaway series and the Hiawatha B_{21}hir showed progressively lower values of extractable Fe with increasing reagent concentration, while extractable Al increased slightly.

Effect of extraction time and shaking treatments: Some selected spodic horizon samples were subjected to 0.1M solution of Na_2-NTA and Na_2-EDTA for three different

Table 4. Effects of concentration of extractants on the extraction of Fe and Al from soils

Soil series	Horizon	Extractants and concentration									
		Na_2-NTA						Na_2-EDTA			
		0.1M		0.2M		0.5M		0.1M		0.2M	
		Fe%	Al%	Fe%	Al%	Fe%	Al%	Fe%	Al%	Fe%	Al%
Kinross	B_{21}hir	trace	.08	.04	.10	trace	.03	trace	.10	.03	.15
Saugatuck-AuGres	B_{21}hir	.20	.51	.18	.49	.19	.54	.13	.33	.10	.38
AuGres-Croswell	B_{21}hir	.29	.33	.26	.37	.27	.29	.11	.20	.12	.19
Croswell-Graycalm	B_{21}hir	.16	.23	.18	.20	.18	.21	.05	.14	.05	.10
Rubicon	B_{21}ir	.23	.41	.21	.45	.21	.39	.10	.20	.10	.18
Rubicon	ortstein	.11	.19	.11	.21	.10	.20	.05	.11	trace	.10
Hiawatha	B_{21}hir	.56	.25	.48	.26	.42	.28	.51	.21	.45	.28
Onaway	B'_{22}t	.40	.12	.38	.14	.26	.15	.16	.06	.12	.10
Munising	B_{21}hir	.48	.47	.46	.49	.44	.44	.50	.53	.51	.59
Munising	B_3X	.07	.07	trace	.09	.05	.03	.04	.06	trace	.06
mean		.25	.26	.23	.28	.21	.26	.17	.19	.15	.21
standard error		±.009	±.008								

extraction times. The first group was shaken continuously for a period of fourteen hours by means of a mechanical shaker. The second group was shaken occasionally by hand for the same period of time. The third group was shaken by hand occasionally for a period of five days (120 hrs.). Na_4-P_2O_7 was also used as an extractant in the first group. The mixtures of soil and solutions were centrifuged after each specified extraction period and the clear extracts were analyzed for Fe and Al. The results of this experiment are shown in Table 5.

The data reveals that in general the fourteen hours of occasional shaking treatment b, resulted in lower yields of both extractable Fe and Al from these soil samples. Extraction time of 120 hours, treatment c, caused the greatest extraction of Fe and Al, and finally the fourteen hours continuous shaking time, treatment a, released intermediate amcunts of extractable Fe and Al. The effects of the time of contact between soil and extractant, as well as shaking duration, are most diverse in the amounts of Fe and Al extracted from the better drained soils with stronger spodic horizon development. Furthermore, these results suggest that although both Na_2-NTA and Na_2-EDTA have extracted more Fe and Al after 120 hours extraction time, the rate of increase of Fe extraction is substantially higher than that of Al.

Table 5. Effect of shaking and extraction time on the amount of Fe and Al extracted by three 0.1M chelating agents

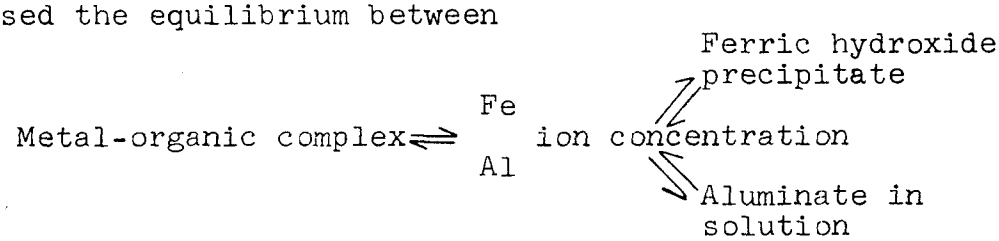
Chelating agent		Extractants, extraction times and shaking treatments													
		$Na_4P_2O_7$		Na_2NTA						Na_2EDTA					
Extraction time		14 hr[a]		14 hr[a]		14 hr[b]		120hr[c]		14 hr[a]		14 hr[b]		120hr[c]	
Soil Series	Horizon	Fe%	Al%	Fe%	Al%	Fe%	Al%	Fe%	Al%	Fe%	Al%	Fe%	Al%	Fe%	Al%
Kinross	$B_{22}hir$	tr.	.06	tr.	.08	tr.	.08	.08	.12	tr.	.09	tr.	.05	.07	.16
Saugatuck-AuGres	$B_{21}hir$	.19	.39	.20	.51	.24	.49	.36	.58	.13	.33	.10	.25	.19	.39
AuGres-Croswell	$B_{21}hir$	.24	.29	.29	.33	.31	.29	.38	.39	.11	.20	.14	.20	.29	.21
Croswell-Graycalm	$B_{21}hir$	.12	.18	.16	.23	.20	.21	.29	.30	.05	.14	tr.	.10	.15	.20
Rubicon	$B_{21}ir$	.15	.24	.23	.41	.15	.36	.48	.50	.10	.20	.05	.18	.21	.28
Hiawatha	$B_{21}hir$	.51	.26	.56	.25	.47	.15	.85	.29	.51	.21	.32	.17	.66	.31
Onaway	$B_{21}ir$	.40	.30	.43	.28	.38	.21	.91	.35	.22	.21	.17	.17	.30	.24
Munising	$B_{21}hir$	.47	.60	.48	.47	.40	.38	.75	.62	.50	.53	.31	.42	.67	.56
mean		.26	.29	.29	.32	.26	.27	.51	.39	.20	.24	.14	.19	.32	.29
standard error		±.03	±.01												

(a) Overnight, 14 hours, shaking in a reciprocal shaker
(b) Occasional shaking overnight, 14 hours
(c) Occasional shaking for a period of 5 days, 120 hours

Effect of pH of the extractants: The Na_5-DPTA solution at its natural pH of 12, as well as at pH's of 7 and 10, were applied to soils. (HCl was used to adjust the pH to 7 and 10.) The amounts of Fe and Al were determined in the extracts. Carbon was determined in the soil before and after extraction and the difference was recorded as the dispersed organic carbon. The results are given in Table 6.

The data reveals a general trend of increasing amount of extractable Fe, Al and organic carbon with increase of the pH of the extractant. However, the natural pH of 12 of Na_5-DPTA appeared to be too high to detect any Fe in solution.

These results are in agreement with the study of Tinsley and Salam (1961) in which they suggest that as pH is raised the equilibrium between



is likely to be displaced to the right with consequent increase in solubility of the organic complex.

The results obtained from the preliminary studies make obvious the need for some standard procedure as to the effect of extraction time, reagent concentration, and pH. Even though the longer time of contact between reagent and

Table 6. The effect of the pH of 0.1M Na_5-DPTA solutions on the extractability of Fe, Al and organic carbon of soil samples

Soil series	Horizon	Na_5-DPTA								
		pH = 7			pH = 10			pH = 12		
		Fe%	Al%	c%*	Fe%	Al%	c%	Fe%	Al%	c%
Kinross	B_{22}hir	tr.	.08	.08	tr.	.06	-	tr.	.04	.12
Saugatuck-AuGres	B_{21}hir	.12	.30	.89	.15	.41	.97	tr.	.53	1.49
AuGres-Croswell	B_{21}hir	.09	.19	.32	.21	.30	.44	tr.	.34	.50
Croswell-Graycalm	B_{21}hir	.04	.12	.10	.10	.19	-	tr.	.26	-
Rubicon	B_{21}ir	.09	.21	.10	.18	.27	.20	tr.	.44	.25
Hiawatha	B_{21}hir	.49	.16	.51	.58	.20	.68	tr.	.22	.97
Onaway	B_{21}ir	.20	.20	.37	.33	.47	.48	tr.	.41	.42
Munising	B_{21}hir	.49	.53	1.10	.40	.56	1.90	tr.	.49	2.13
means		.19	.22	.43	.24	.31	.58		.34	.74
standard error for pH class ±.07										

*The percentages of extracted carbon is based on the total dry combustion values of original soil and after extraction. Dashes indicate negative carbon values.

soil material appeared to result in higher amounts of extractable Fe and Al, the fourteen hours of continuous shaking for practical purposes is more suitable. The reagent concentration of 0.1M also proved to be more efficient since the sensitivity of the atomic absorption unit drops with increasing concentration of the reagent. Finally, the pH has a pronounced influence on the extractability of illuvial materials, as is evident from the study with DPTA. However, it seemed desirable to use the reagents at the natural pH of their solutions and to study the effect of a range of pH's as well as the extractants themselves.

Considering the above preliminary studies, Bascomb's (1968) procedure was adapted and slightly modified by substituting different organic chelating agents with different pH's for the K-pyrophosphate. Also, sodium was used as an accompanying cation with all the extracting reagents. The discussion of the results follows.

Principal Studies

pH of the extracting solutions before and after contact with the soil samples: The extracting solutions used in this tudy provide a range of pH's. These are pH 3.2, 4.6, 10, and 12, corresponding to 0.1M solutions of Na_2-NTA, Na_2-EDTA, Na_4-pyrophosphate, and Na_5-DPTA, respectively. The Na_5DPTA solution was buffered strongly enough to maintain a constant pH even after being in contact with the soil

samples studied, Table 7. The Na-pyrophosphate solutions maintained their initial pH values within 0.3 pH unit. However, the A_1 horizon of the Hiawatha and Munising series lowered the pH of the Na_4-pyrophosphate extracting solutions 0.5 and 0.7 units, respectively. Those horizons did not change the pH of the other extracting solutions appreciably. The pH's of the Na_2-NTA and Na_2-EDTA extractants usually remained within 0.1 pH of their original reactions. The Na_2-NTA pH was raised from 3.2 to 3.6 and the Na_2-EDTA pH was raised from 4.6 to 4.7 after contact with the argillic horizon of the Onaway soil series.

The rise in pH of extracting solutions (Na_2-NTA and Na_2-EDTA) upon contact with the argillic horizon of the Onaway soil series may be attributed to attack on silicate minerals by solutions of such low pH's and consequent release of hydroxyl ions to the environment.

Color of the soil extracts: The Munsell notations for extract colors are shown in Table 8. The A_1 horizon extracts were considerably lighter in color as compared to the spodic horizon extracts. However, the Na_2-NTA extracts were more yellowish in color (with hues of 2.5Y and 5Y) while the Na_2-EDTA, Na_4-pyrophosphate, and Na_5-DPTA extract colors ranged from the yellowish brown to dark brown. The poorly drained soils (Kinross and Saugatuck) had colors mostly in brownish yellow (10YR 6/6) with Na_2-NTA and

Table 7. pH values of the extracting solutions before and after contact with soil samples

Soil series	Horizon	Extractant (initial pH)		
		Na_2NTA (pH=3.2)	Na_2EDTA (pH=4.6)	$Na_4P_2O_7$ (pH=10)
Kinross	$B_{21}h$	3.2	4.4	9.8
	$B_{22}hir$	3.2	4.4	9.9
Saugatuck-AuGres	$B_{21}hir$	3.3	4.6	10.1
	$B_{22}hir$	3.3	4.5	9.9
	$IIB_{21}hir'$	3.3	-	10.0
	IIBhir'm	3.2	4.5	10.0
AuGres-Croswell	$B_{21}hir$	3.2	4.6	10.2
	$B_{22}hir$	3.3	4.6	10.3
Croswell-Graycalm	UPP.$B_{21}hir$	3.3	4.6	10.2
	low $B_{21}hir$	3.2	4.5	10.2
	$B_{22}hir$	3.1	4.5	10.3
Omega	B_{22}	3.3	4.6	10.3
Eastport	B_{21}	3.2	4.5	10.3
Rubicon	A_1	3.2	4.4	9.7
	$B_{21}ir$	3.3	4.6	10.1
	$B_{22}ir$	3.1	4.6	10.2
	ortstein	3.2	4.5	10.2
Hiawatha	A_1	3.2	4.4	9.5
	A_2	3.3	4.5	10.0
	$B_{21}hir$	3.2	4.6	9.9
	$B_{22}ir$	3.3	4.5	10.2
Onaway	A_2	3.2	4.5	9.8
	$B_{22}ir$	3.3	4.5	10.0
	$B_{22}ir$	3.3	4.4	10.1
	$B_{22}t$	3.6	4.7	10.1
Munising	A_1	3.2	4.4	9.3
	A_2	3.2	4.4	9.9
	$B_{21}hir$	3.3	4.6	9.9
	$B_{22}ir$	3.3	4.6	10.1
	B_3x	3.2	4.5	10.0

Na_2-EDTA, while yellow colors were dominant with Na_4-pyrophosphate and Na_5-DPTA. The color of the highly developed spodic horizons (Hiawatha and Munising) ranged from strong brown (7.5 YR 5/6) to yellowish red (5Y 5/6). The less developed spodic horizons (AuGres-Croswell, Croswell-Graycalm and Rubicon) were mostly white (5Y 8/2-8/1). In general, Na_5-DPTA colors were mostly yellow (2.5Y-5Y) while the other extractants were comparable in color.

Fe extraction results: In general the Na_2-NTA chelating agent resulted in the extraction of substantial amounts of extractable Fe from most of the soil samples studied (Table 9). Na_2-EDTA extracting solution yielded very low amounts of Fe, and Na_4-pyrophosphate extracted somewhat less than Na_2-NTA. The methods were most diverse in the amounts of Fe extracted from the Rubicon profile.

Na_5-DPTA extracts contained trace amounts of Fe (not shown in Table 9). As discussed earlier in the preliminary study of the effect of pH on the extractability of Fe, Al, and C, the low quantity of iron in these extracts was due to the high pH of this extractant, which would have caused the precipitation of Fe as $Fe(OH)_3$.

If only the effect of pH were to be considered, the data reveals that the low pH extractants have resulted in the highest amounts of extractable Fe; yet the Na_4-pyrophosphate (pH=10) has also extracted as much Fe as Na_2-EDTA (pH=4.6). Furthermore, the Na_2-NTA extractable Fe is

Table 8. Color of the spodic B extracts by different extractants

Soil series	Horizon	Munsell notations — Extractant: Na_2NTA	Na_2EDTA	$Na_4P_2O_7$	Na_5DPTA
Kinross	$B_{21}h$	10YR7/8	7.5YR5/8	10YR6/8	2.5Y7/8
	$B_{22}hir$	10YR7/8	10YR6/8	2.5y7/8	2.5Y7/6
Saugatuck-AuGres	$B_{21}hir$	10YR6/8	10YR6/8	10YR6/8	2.5Y7/6
	$B_{22}hir$	10YR7/8	10YR6/8	2.5Y7/8	2.5Y7/8
	$IIB_{21}hir'$	10YR6/8	10YR6/8	2.5Y7/8	2.5Y7/8
	IIBhir'm	2.5Y7/8	2.5Y7/8	2.5Y7/8	2.5Y7/8
AuGres-Croswell	$B_{21}hir$	2.5Y7/8	5Y7/6	2.5Y7/6	2.5Y7/8
	$B_{22}hir$	-	5Y8/1	5Y7/4	5Y8/4
Croswell-Graycalm	$UPPB_{21}hir$	-	5Y8/2	5Y8/3	5Y8/4
	low $B_{21}hir$	5Y7/8	5Y7/6	5Y7/6	5Y7/6
	$B_{22}hir$	5Y8/2	5Y8/1	5Y8/2	5Y8/2
Rubicon	A_1	5Y7/6	7.5YR5/8	5YR3/3	5YR3/4
	$B_{21}ir$	2.5 7/6	5Y7/6	2.5Y6/8	5Y7/6
	$B_{22}ir$	5Y8/3	5Y8/1	5Y8/1	5Y8/2
Hiawatha	A_1	5Y8/3	2.5Y7/6	10YR5/6	2.5Y5/6
	$B_{21}hir$	7.5YR5/6	7.5YR5/8	7.5YR5/6	2.5Y6/8
	$B_{22}ir$	2.5Y7/8	2.5Y7/8	2.5Y6/6	5Y7/8
Onaway	$B_{21}ir$	2.5Y6/8	2.5Y6/8	10YR7/8	2.5Y7/8
	$B_{22}ir$	2.5Y7/8	2.5Y7/8	2.5Y7/6	5Y7/8
Minising	A_1	2.5Y7/6	10YR6/8	5YR3/4	7.5YR4/4
	$B_{21}hir$	5YR5/8	5YR5/8	10YR5/6	2.5Y6/8
	$B_{22}ir$	2.5Y7/8	2.5Y7/8	10YR6/8	5Y7/8

commonly not significantly higher than Na_4-pyrophosphate extractable Fe, but rather comparable to them.

The chelating powers of the reagents are different. Martell and Calvin (1954) give the stability constants of NTA with Fe^{++} as 8.82 and that of EDTA with Fe^{++} as 14.33. Therefore, EDTA is capable of forming more stable Fe chelates compared to NTA. In addition, EDTA possesses two donor groups in the structure which render a stronger ability to chelate metals. However, the data obtained for the soils studied here show more extraction by NTA than EDTA in all samples.

Na_5-DPTA has three donor groups, the highest number of donor groups among the three organic chelating agents used in the study. Therefore, it would be expected to chelate metals most readily. The stability constant of Na_5-DPTA with Fe^{++} is 16.5. As mentioned earlier, the high pH value may have masked the chelatability of this extractant. Its extraction of iron was greatly improved at pH 10. Its ability to chelate aluminum will be discussed later.

Na_4-pyrophosphate is an inorganic chelating agent and has resulted in comparable amounts of extractable Fe as Na_2-NTA and Na_2-EDTA. With the above generalizations as background, the results obtained for each of the profiles studied are shown in Table 9 and Figure 2 and will be examined in the following paragraphs.

Table 9. Percent total carbon and extractable iron and aluminum content of soil samples with different extracting solutions (chelating agents)

Soil series	Horizon	Lab #	% total carbon	Extractant: 0.1M Na_2-NTA pH=3.2 %Fe	0.1M Na_2-NTA pH=3.2 %Al	0.1M Na_2-EDTA pH=4.6 %Fe	0.1M Na_2-EDTA pH=4.6 %Al	0.1M Na_4PPO_4 pH=10 %Fe	0.1M Na_4PPO_4 pH=10 %Al	0.1M Na_5-DPTA pH=10 %Fe	0.1M Na_5-DPTA pH=10 %Al
Toposequence:											
Kinross	$B_{21}h$	1	1.11	tr.	.09	tr.	.10	tr.	.08	-	.04
	$B_{22}hir$	2	.66	tr.	.08	tr.	.09	tr.	.06	-	.04
Saugatuck-AuGres	$B_{21}hir$	3	3.27	.20	.51	.13	.33	.19	.39	-	.53
	$B_{22}hir$	4	1.45	.11	.32	.09	.25	.09	.26	-	.41
	$IIB_{21}hir'$	5	1.46	.02	.40	.02	.32	.02	.33	-	.48
	IIBhir'm	6	.69	.01	.16	.01	.15	.02	.19	-	.16
AuGres-Croswell	$B_{21}hir$	7	1.29	.29	.33	.11	.20	.24	.29	-	.34
	$B_{22}hir$	8	.59	.15	.22	.04	.10	.09	.18	-	.29
Croswell-Graycalm	$UPPB_{21}hir$	9	.53	.16	.23	.05	.14	.12	.18	-	.26
	low $B_{21}hir$	10	.58	.18	.21	.12	.16	.18	.20	-	.23
	$B_{22}hir$	11	.25	.09	.13	.03	.07	.07	.10	-	.23
Range of spodic development:											
Omega	B_{22}	12	.44	.09	.21	.01	.07	.02	.12	-	.31
Eastport	B_{21}	13	.27	.12	.10	.07	.05	.14	.10	-	.26
Rubicon	A_1	14	2.56	.04	.04	.02	.03	.05	.03	-	.02
	$B_{21}ir$	15	1.07	.23	.41	.10	.20	.15	.24	-	.44
	$B_{22}ir$	16	.33	.09	.24	.01	.06	.03	.12	-	.31
	ortstein	17	.62	.11	.19	.05	.11	.08	.18	-	.24
Hiawatha	A_1	18	5.40	.05	.02	.03	.02	.03	.01	-	.01
	A_2	19	.79	.05	.03	.04	.02	.07	.02	-	.01
	$B_{21}hir$	20	2.15	.56	.25	.51	.21	.51	.26	-	.22
	$B_{22}ir$	21	1.38	.27	.48	.10	.26	.21	.35	-	.41
Onaway	A_2	22	1.27	.02	.02	.01	.01	.04	.02	-	.01
	$B_{21}ir$	23	1.48	.43	.28	.22	.21	.40	.30	-	.41
	$B_{22}ir$	24	1.04	.34	.16	.17	.11	.30	.12	-	.22
	$B_{22}t$	25	1.28	.40	.12	.16	.06	.11	.05	-	.29
Munising	A_1	26	5.49	.06	.02	.04	.03	.06	.02	-	.01
	A_2	27	1.36	.06	.02	.04	.02	.06	.01	-	.01
	$B_{21}hir$	28	3.19	.48	.47	.50	.53	.47	.60	-	.49
	$B_{22}ir$	29	1.92	.34	.54	.20	.44	.33	.46	-	.49
	B_3X	30	.45	.07	.07	.04	.06	.07	.07	-	.05

A. Toposequence of profiles:

Kinross: The $B_{21}h$ and $B_{22}hir$ horizons of Kinross series yielded negligible amounts of Fe upon extraction with all of the extracting solutions used in this study. These findings are in agreement with a recent study by Collins (1971) in which the author was able to detect only traces of Fe in his pyrophosphate extracts. This profile is located twenty feet out into a leather-leaf-sphagnum bog on a nearly level area with poor drainage. The water table is commonly at 6" below the surface during the growing season. It was developed in reducing conditions with low pH where all the iron may be in the ferrous forms and is leached away.

Saugatuck-AuGres: The amount of extractable Fe released by all extractants were considerably higher in the upper spodic horizons and decreased with depth. Na_2-NTA and Na_4-pyrophosphate extracted the highest amount of iron from $B_{21}hir$ and $B_{22}hir$, while Na_2-EDTA extracted less from the upper $B_{21}hir$ horizon. The amounts of Fe released by the three reagents were almost the same for both the lower B_2 and cemented spodic horizons, $IIB_{21}hir'$ and IIBhir'm. Considering the moisture regime of the profile and the fact that the internal drainage is imperfect, with the water table at an average depth of 28" during the growing season, the data clearly shows that the lower cemented horizons from 16"-33" are less aerated as the result of the presence of a

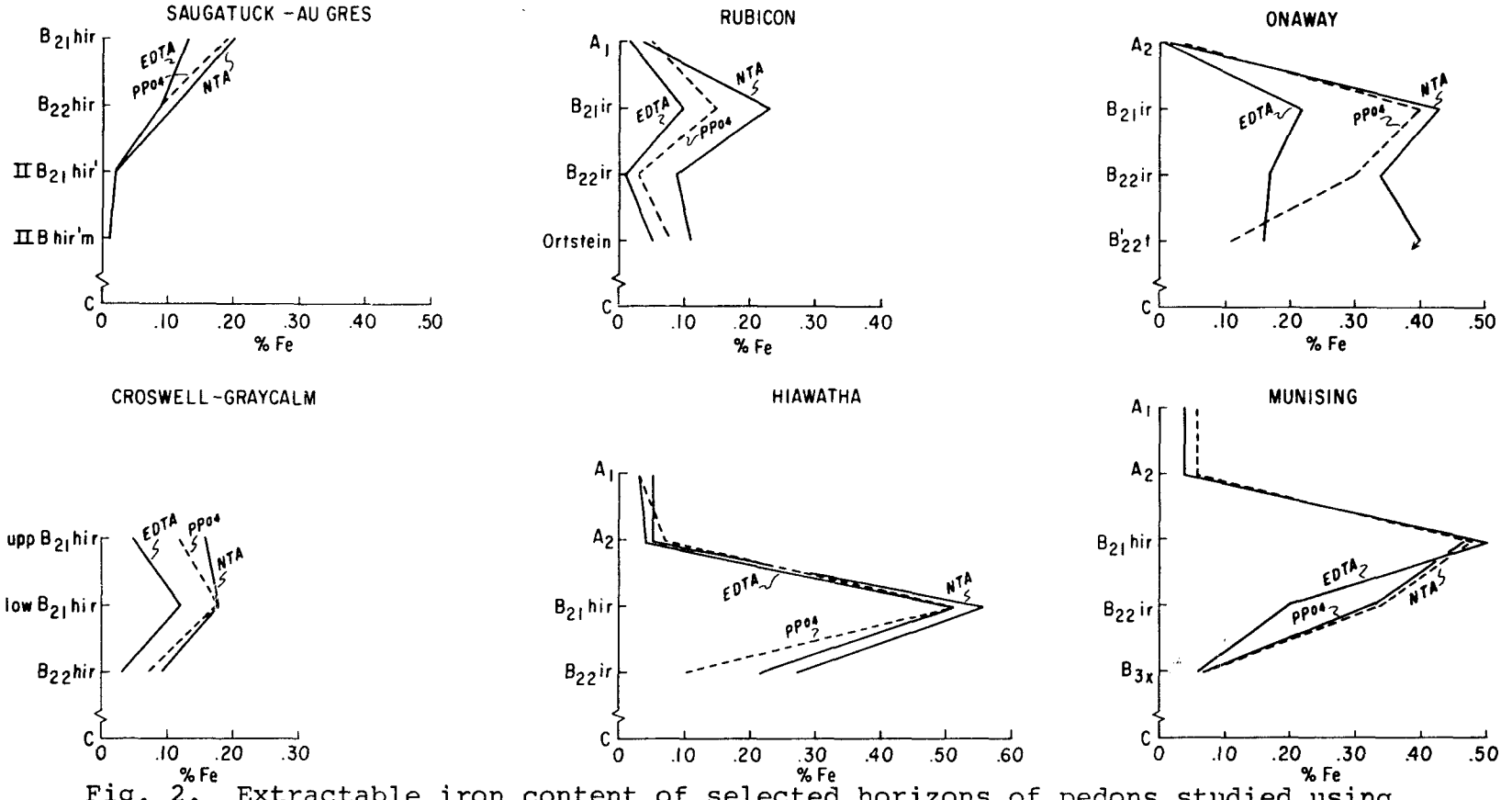


Fig. 2. Extractable iron content of selected horizons of pedons studied using different extractants.

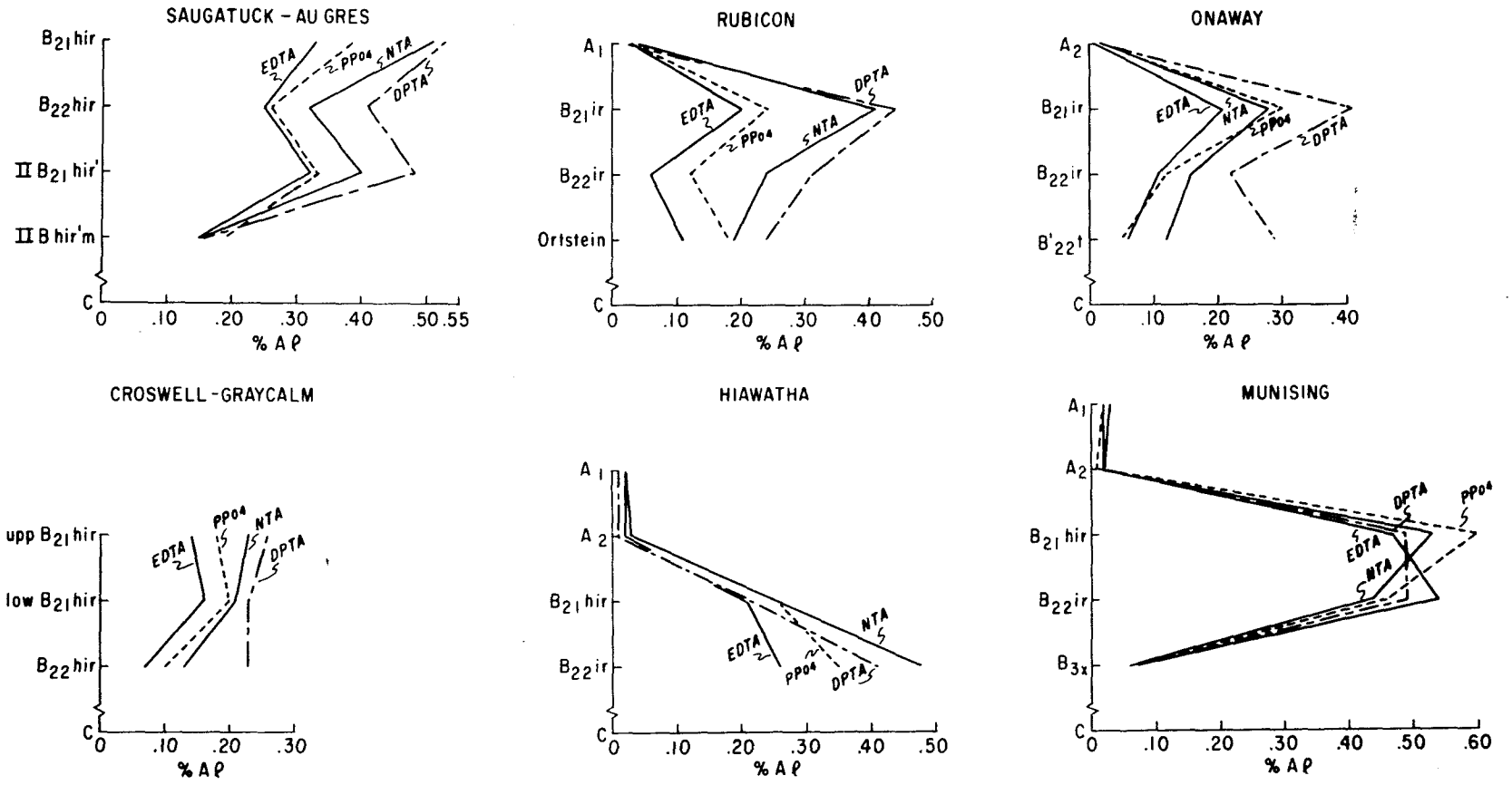


Fig. 3. Extractable aluminum content of selected horizons of pedons studied using different extractants.

water table. Consequently, the prevailing reducing conditions have resulted in lower Fe content. The Fe maxima is in the upper spodic development with finer texture. The extractable iron in this profile decreased with depth in the spodic horizon.

AuGres-Croswell: Among the three extractants the Na_2-NTA extracted the largest amount of iron. Na_4-pyrophosphate and Na_2-EDTA released the intermediate and lowest amounts of Fe, respectively. The site where the sample was taken is a better drained location with a drainage class of imperfect to moderately well drained. The depth of the water table averages 36" during the growing season. The Fe maximum occurs in the spodic horizon somewhere in the upper B_2hir and decreases in the lower part of this horizon.

Croswell-Graycalm: The Fe maximum occurs in the lower B_{21}hir in the location from which this sample was taken. The Na_2-NTA and Na_4-pyrophosphate released the same amounts of iron from this horizon while Na_2-EDTA extracted the lowest amounts of Fe. This profile is located at a better drained site in this toposequence. It is moderately well drained with the water table at an average depth of 58" during the growing season. The extraction of Fe is lower in the B_{22}hir horizon.

Summary: The extraction data overall shows a high accumulation of Fe in all the spodic horizons of the soils

in this toposequence except the very poorly drained member, Kinross. The maximum accumulation is in the somewhat poorly drained members (Collins, 1971).

B. Profiles representing range of spodic development:

The second group of soils includes a range of spodic horizon development from the weakest to the strongest development in Michigan (Lietzke, 1969). The results of the Fe extraction for these soils are summarized in the following paragraphs.

Omega: The B_{22} horizon of Omega series contained a large proportion of Na_2-NTA-extractable Fe as compared to Na_2-EDTA and Na_4-pyrophosphate. The latter two extractants released only very little iron from this particular horizon.

Eastport: B_{21} extractable Fe content with the chelating agents used in this study was generally higher in comparison with Omega B_{22}. The extractability of iron by these reagents in a decreasing order is as follows:

$$Na_4\text{-pyrophosphate} = Na_2\text{-NTA} > Na_2\text{-EDTA}$$

Rubicon: A_1, $B_{21}ir$, $B_{22}ir$ and ortstein horizons of this soil series were subjected to extraction with the chelating agents. Except for the A_1 horizons where both Na_4-pyrophosphate and Na_2-NTA yielded similar small quantities of extractable Fe, the extraction pattern followed the same general trend in that Na_2-NTA extracted the highest quantity

of Fe, Na_2-EDTA the lowest amount, and Na_4-pyrophosphate intermediate quantities. The amount of extractable Fe from the ortstein horizon lies between that of $B_{21}ir$ and $B_{22}ir$ horizons. Ortstein occurs at a depth ranging from 9" to 27" with chunks or tongues 1 1/2"-3" thick, as described by Whiteside and Johnson (1967). This soil gives rise to two Fe maxima due to the presence of ortstein, in which extractable Fe content of the second zone of maxima is considerably lower than the first Fe maxima in the $B_{21}ir$ horizon.

Hiawatha: The per cent Fe extracted from each horizon of this soil is quite similar for the different extractants. The A_1 and A_2 horizons yielded the lowest values while the maximum extractable Fe occurred in the $B_{21}hir$ horizon where the spodic horizon expression is quite pronounced in the field. The differences in the amounts of extractable Fe obtained with the solutions used in this study were quite noticeable in the $B_{22}ir$ horizon. The order of extraction is shown below:

$$Na_2\text{-NTA} = Na_4\text{-pyrophosphate} > Na_2\text{-EDTA}$$

This soil is well drained and has been classified as a Typic Haplorthod according to 1967 classifications. The spodic characteristics and morphology are easily observable in the field. The high content of extractable Fe also confirms this strong development.

Onaway: The A_2, $B_{21}ir$, $B_{22}ir$, and $B'_{22}t$ horizons of this soil series were studied for extractable Fe content. The results showed two Fe maxima. These occurred in $B_{21}ir$ and the argillic horizon $B'_{22}t$ when Na_2-NTA was used as the extractant. The other two extractants, Na_4-pyrophosphate and Na_2-EDTA, resulted in only one Fe maximum in the $B_{21}ir$ horizon. Na_2-EDTA extracted the lowest amount of Fe from the B_2ir, while similar, larger quantities of extractable Fe were obtained with Na_4-pyrophosphate and Na_2-NTA solutions. As mentioned earlier, the NTA-extractable Fe content from $B'_{22}t$ was considerably higher than the amount extracted with the other solutions. This may be due to the fact that the clay particles in this particular horizon (clay content = 24.9%) were more seriously affected by this acid solution. Other forms of Fe, in addition to those characteristic of spodic horizons, were extracted as well. The other solutions, with higher pH's, were more specific as to the form of iron being extracted.

Munising: Except for the $B_{22}ir$ horizon, which yielded different quantities of extractable Fe with the extractants used in the study, all the other horizons of this soil resulted in the release of similar quantities of Fe with the three chelating agents used. The A_1, A_2 and fragipan B_3x contained the lowest extractable Fe contents. The $B_{21}hir$ horizon contained the highest amount. Therefore, an

Fe maxima occurred in this horizon near the top. This soil has more clay content throughout the profile as compared to Hiawatha, yet the extractable Fe content of the spodic horizon is quite comparable to that of Hiawatha.

Aluminum extraction results: The extraction of Al with the chelating agents used in this study follow the same general pattern as that of Fe, Table 9, Figure 3, except that substantial quantities were extracted by Na_5-DPTA.

In contrast to Fe extraction, a considerable amount of Al was extracted from almost all the soils with a high pH Na_5-DPTA solution. This was particularly true of the Onaway, Saugatuck-AuGres, Rubicon, and Croswell-Graycalm pedons. Na_2-NTA extracted more Al as compared to Na_4-pyrophosphate and Na_2-EDTA extractants. However, the magnitude of differences are markedly higher with the $B_{21}ir$ and $B_{22}ir$ horizons of Rubicon and Croswell-Graycalm pedons. The other pedons do not show a consistent difference in the amount of extractable Al with the different extractants, although there exists a very pronounced variation in the amount of extractable Al from horizon to horizon within a profile. This relationship is evident in the lower B_2ir horizons. The profile variations will be discussed in more detail in the following paragraphs.

Data on solubility of Al in solutions at different pH values is given by Magistad (1925), Jackson (1961), and Rich (1960). The suggested behavior of Al in response to various

pH values indicate that in strongly acid solution the Al exists as the trivalent cation complex with six water molecules in six coordinations, forming $Al(H_2O)_6^{+3}$. Jackson (1961) designates the resulting trivalent ion complex "aluminohexahydronium". With increasing pH the H_2O groups lose an H^+ ion to form an OH^- ion. This results in di- or mono-valent hydroxy-Al cations with the formula $Al(OH_2)_5(OH)^{+2}$ and $Al(OH_2)_4(OH)_2^{+1}$, respectively. With subsequent increases in pH the precipitation $Al(OH)_3(OH_2)_3$ will result. However, further increase in pH will solubilize Al by formation of $Al(OH)_6^{-3}$. Therefore the higher amounts of Al extracted by Na_5-DPTA may be a reflection of the high pH associated with this extractant.

The amount of Al extracted by all the chelating agents markedly exceeds the corresponding amounts of extractable Fe. This is in agreement with Martin and Reeve (1957). These authors postulate that the higher content of extractable Al may be a reflection of the excess of total Al over total Fe present in all soils. Consequently it is difficult to assume that Al has a predominant influence in combining with the organic fraction.

The free iron oxide contents and the total exchangeable Al of some of the pedons used in the study, determined by SCS laboratory, are shown in Table 10. The orthophenanthroline colorimetry and fluoride titration methods are used for Fe

oxide and exchangeable Al determination, respectively. The data shows that, except for the Onaway B_{21}ir and B_{22}ir horizons, the spodic B horizons have higher contents of Al compared with Fe. Al exceeds Fe six to seven times in the case of Munising B_{21}hir and B_{22}ir. These results may serve to confirm the validity of Martin and Reeve's postulate.

The results of the extractable Al for all the pedons are further discussed in the following paragraphs.

A. Toposequence of profiles:

Kinross: The B_{21}h and B_{22}hir horizons released more Al upon extraction with the chelating agents as compared with Fe, but the extractable Al was also lowest in this poorly drained member of the toposequence. The extractable Al of this soil is comparable with all four extractants used. From the very low amounts of extractable Fe it seems that Fe plays little or no part in stabilizing organic matter in this poorly drained soil. It is therefore concluded that Al is the "active" metal involved in stabilizing the organic fraction in the spodic horizon of this soil.

Saugatuck-AuGres: The amount of Al extracted by the chelating reagents is quite diverse. The B_{21}hir released more Al than any other horizon. The effect of the extracting solutions on the amount of extractable Al is as follows:

Al-DPTA > Al-NTA > Al-pyrophosphate > Al-EDTA

Table 10. Percent free iron oxide and total exchangeable Al of some of the soil pedons used in the study by orthophenanthroline colorimetry and fluoride titration methods

Soil series and horizon		Total iron oxide as % Fe	% Exchangeable Al
Omega	B_{22}	0.40	0.40
Eastport	B_{21}	0.30	0.10
Rubicon	A_1	0.20	0.60
	B_{21}ir	0.50	1.40
	B_{22}ir	0.20	0.40
	ortstein	0.20	0.50
Hiawatha	A_1	0.40	0.10
	A_2	0.40	0.30
	B_{21}hir	1.10	2.40
	B_{22}ir	0.60	1.90
Onaway	A_2	0.50	0.40
	B_{21}ir	1.70	1.40
	B_{22}ir	1.40	1.00
	B'_{22}t	2.00	trace
Munising	A_1	0.40	0.30
	A_2	0.40	0.90
	B_{21}hir	1.00	6.10
	B_{22}ir	0.60	4.00
	B_3X	0.40	1.20

The horizon with the next highest extractable amount of Al was $IIB_{21}hir'$. The $B_{22}hir$ has an intermediate amount of extractable Al, while the IIBhir'm yielded the least amount of Al upon extraction. The data suggest that Al was lost from the $B_{22}hir$ horizon and accumulated in the $IIB_{21}hir'$, probably complexed and fixed with organic matter. The $B_{22}hir$ and $IIB_{21}hir'$ extractable Al contents were quite diverse upon DPTA, NTA and pyrophosphate extraction, while EDTA extracted the same amount of Al as pyrophosphate.

AuGres-Croswell: The DPTA extractable Al from the $B_{21}hir$ and $B_{22}hir$ horizons were greatest, while EDTA extracted the least amount of Al. The other two extracting solutions resulted in intermediate amounts of extractable Al. In every case the $B_{21}hir$ had more extractable Al compared with the lower $B_{22}hir$ horizon.

Croswell-Graycalm: The maximum extractable Al occurred in the lower $B_{21}hir$ when EDTA and pyrophosphate were used as the extracting agents, while the maximum occurred in the upper $B_{21}hir$ with DPTA and NTA. In general, the DPTA solution extracted the highest amount of Al from all horizons, followed by NTA, pyrophosphate, and EDTA, in decreasing order. The amount of Al extracted was less in this well drained member of the toposequence than in the somewhat poorly drained member.

B. Profiles representing range of spodic development:

Omega: The B_{22} had a high amount of DPTA extractable Al. The NTA extractable Al was intermediate, while EDTA and pyrophosphate extracted lower amounts of Al.

Eastport: The B_{21} horizon had a high DPTA extractable Al content as compared with other extracting solutions. NTA and pyrophosphate extracted the same intermediate amounts of Al from this horizon, and EDTA the least.

Rubicon: The A_1, $B_{21}ir$, $B_{22}ir$ and an ortstein were subjected to extraction by the chelating agents. The A_1 had a trace amount of extractable Al with all of the reagents used. Maximum Al occurred in the $B_{21}ir$ horizon. The $B_{22}ir$ contained less extractable Al compared to the upper $B_{22}ir$. Ortstein had an intermediate amount of extractable Al. This drop in the amount of Al in the $B_{22}ir$ and its subsequent increase in the ortstein was only evident with EDTA and pyrophosphate extractions. DPTA and NTA showed a continuous decrease in the amount of extractable Al from the $B_{22}ir$ horizon downward. DPTA and NTA extracted more Al from the $B_{21}ir$ horizon compared to Al extracted from the same horizon by EDTA and pyrophosphate.

Hiawatha: The A_1 and A_2 horizons contained traces of extractable Al with all the extracting agents used. The $B_{21}hir$ had the less extractable Al than the lower $B_{22}ir$. NTA resulted in the maximum extractable Al from the $B_{22}ir$,

followed by DPTA, pyrophosphate, and EDTA in decreasing order. The data suggest that the Al had been translocated deeper in this profile than in the other pedons studied, where the extractable Al usually decreases with depth.

Onaway: The A_2 horizon contained traces of extractable Al with all the extracting solutions. The maximum extractable Al occurred in the $B_{21}ir$; the lowest in the $B'_{22}t$, an argillic horizon; and intermediate extractable Al in the $B_{22}ir$. In general, the DPTA extractable Al content was considerably higher than the corresponding EDTA extractable Al, while pyrophosphate and NTA solutions released intermediate amounts of Al.

Munising: The A_1, A_2, and the fragipan horizons contained very low quantities of extractable Al. The highest amount of Al occurred in the $B_{21}hir$ and $B_{22}ir$ horizons. The distribution of extractable Al depended upon the extracting agent used. Upon extraction with Na_4-pyrophosphate and Na_2-EDTA, the maximum occurred in the $B_{21}hir$, while NTA resulted in maximum extractable Al in the $B_{22}ir$. DPTA extracted the same amount from both the $B_{21}hir$ and $B_{22}ir$ horizons.

Carbon extraction results: The total carbon content of the soils used, before extraction with different chelating agents, are shown in Table 9. (Due to the low pH of the soil samples and lack of carbonates, the total carbon is taken to

be equal to the organic carbon present in the soil.) The extractable carbon was obtained from the difference in carbon between the non-treated (original) soil and the treated soil, as shown in Table 11. The fact that some carbon measurements were greater after extraction is a peculiarity that will be discussed later. The percent of total carbon extracted by the different extractants are also calculated in Table 11. Where carbon measured did not change or increased with extraction, no figure is given and a dash is substituted.

In addition to spodic horizons, other horizons such as A_1, A_2, ortstein, argillic and fragipan were subjected to extraction by the different chelating agents.

The high organic matter surface horizons, such as Rubicon A_1, Hiawatha A_1, and Munising A_1 have very little extractable carbon. However, the high pH Na_5-DPTA solution extracted as much as 22% of the total carbon from Munising A_1. In general, it can be concluded that the chelating extractants used in this study are not specific to the form of organic matter present in surface soil, as evident by the very low efficiency of extraction of such materials, Table 11. The A_2 horizons used in the study are low in initial carbon content. The Hiawatha A_2 did not yield any extractable carbon. The other A_2 horizons (Onaway and Munising), which have relatively higher contents of organic carbon, yielded small amounts of extractable carbon.

Table 11. Percent of total carbon after extraction, percent extractable carbon, and the percent of total carbon extracted by the different extractants used in this study

Soil series	Horizons	Extractants											
		Na_2-NTA			Na_2-EDTA			$Na_4P_2O_7$			Na_5-DPTA		
		%C after extraction	% ext. C(1)	% of total C ext.(2)									
Kinross	$B_{21}h$	.70	.41	37	.77	.34	30	.73	.38	34	.53	.58	50
	$B_{22}hir$	.39	.27	40	.05	.61	92	.74	-	-	.54	.12	18
Saugatuck-AuGres	$B_{21}hir$	1.15	1.12	49	1.48	.79	34	1.24	1.03	45	.78	1.49	65
	$B_{22}hir$	.67	.81	54	.77	.71	47	.98	.50	33	.73	.70	47
	$IIB_{21}hir$	.62	.84	57	.46	1.00	68	.67	.79	54	.70	.76	52
	IIBhir'm	.20	.49	71	.74	-	-	.62	.07	-	.54	.15	21
AuGres-Croswell	$B_{21}hir$	.62	.67	51	.74	.55	42	.82	.47	36	.79	.50	38
	$B_{22}hir$	.59	-	-	.37	.22	37	.54	.05	-	.49	.10	16
Croswell-Graycalm	$UPPB_{21}hir$	.47	.06	11	.37	.16	30	.70	-	-	.74	-	-
	Low $B_{21}hir$	.58	.30	34	.77	.11	12	.88	-	-	.88	-	-
	$B_{22}hir$	.32	-	-	.37	-	-	.78	-	-	.58	-	-
Omega	B_{22}	.49	-	-	.88	-	-	.82	-	-	.74	-	-
Eastport	B_{21}	.28	-	-	.74	-	-	.71	-	-	.69	-	-
Rubicon	A_1	2.45	.11	4	2.38	.18	6	2.45	.11	4	2.50	.06	2
	$B_{21}ir$	.88	.19	17	1.02	.05	-	1.10	-	-	.82	.25	23
	$B_{22}ir$	.54	-	-	.37	-	-	.86	-	-	.58	-	-
	ortstein	.38	.23	37	.66	-	-	.70	-	-	.66	-	-
Hiawatha	A_1	5.17	.22	4	4.83	.47	8	5.03	.37	6	2.87	2.53	47
	A_2	.78	-	-	.32	-	-	.95	-	-	1.00	-	-
	$B_{21}hir$	.78	1.37	63	1.02	1.13	52	.84	1.21	56	1.18	.97	45
	$B_{22}ir$	1.20	.18	13	.36	1.02	73	.91	.47	34	.74	.64	46
Onaway	A_2	1.25	.02	1	1.13	.14	11	1.20	.07	6	1.16	.11	8
	$B_{21}ir$	.67	.61	41	.78	.70	47	.88	.60	40	1.06	.42	28
	$B_{22}ir$	.62	.42	40	.54	.50	48	1.02	.02	-	1.00	.04	-
	$B_{22}t$	.69	.67	51	.44	.84	65	1.12	.16	12	1.23	.05	-
Munising	A_1	7.47	-	-	4.43	-	-	5.60	-	-	4.28	1.21	22
	A_2	1.19	.17	12	.39	.47	34	1.28	.08	-	1.36	-	-
	$B_{21}hir$	1.11	2.09	65	.85	2.31	72	1.18	2.01	63	1.06	2.13	66
	$B_{22}ir$	.79	1.14	59	.69	1.23	64	.79	1.13	58	.86	1.06	55
	B_3X	.40	.05	11	.24	.21	46	.46	-	-	.79	-	-

(1) Calculated from the difference between the original (Table 9) and the treated samples. Dashes indicate where negative values were recorded.
(2) Percent extractable carbon divided by percent total original carbon (Table 9) x 100.

The only extractant capable of dispersing carbon from the ortstein horizon of the Rubicon pedon was the acidic solution of Na_2-NTA (pH=3.2). Thirty-seven per cent of the total organic carbon of this horizon was extracted by Na_2-NTA. This extractant also resulted in relatively high amounts of Fe and Al from this horizon, as discussed previously. Therefore, Na_2-NTA may have disturbed the association between sesquioxides and organic matter and consequently resulted in higher carbon extraction.

The low pH extractants appeared to be more effective in extracting carbon from the argillic ($B'_{22}t$) horizon of the Onaway pedon. Na_2-EDTA and Na_2-NTA extracted 65% and 51% of the total organic carbon, respectively. Na_4pyrophosphate resulted in extraction of 12% of the total carbon and the highest pH extractant resulted in a very minute amount of extractable carbon. This particular horizon contains about 24.9% clay and it can be postulated that the acidic extractants released organic matter adsorbed on clay surfaces.

Na_2-EDTA appeared to be the most effective extractant of carbon from the fragipan horizon of Munising. Forty-six per cent of the total carbon was extracted by this chelating agent. Na_2-NTA resulted in considerably less extractable organic carbon. The other extractants did not result in dispersion and consequent extraction of organic carbon from Munising fragipan.

In general, the sub-surface horizons initially low in organic carbon content did not respond to the extracting solutions, regardless of their internal drainage or intensity of expression of pedogenic processes. Included among those horizons are Croswell-Graycalm B_{22}hir, Omega B_{22}, Eastport B_{21}, and Rubicon B_{22}ir. The organic carbon content of these soils prior to extraction are .25, .44, .28, and .33, respectively. More organic carbon was detected in these samples after the soils were subjected to different extractants, resulting in negative amounts of extractable organic carbon. The possibility of the adsorption of some of the chelating agents by soil particles does not seem to be valid since these soils contain very little clay particles. It is also evident from the precision of determination on replicates of the same sample that the variation is not sufficient to obscure carbon changes in these soils. The carbon extraction results will be further examined as follows:

Kinross: From 18%-92% of the total carbon of the B_{21}h and B_{22}hir horizons of this soil series was extracted by the chelating agents used in this study. However, Na_4-pyrophosphate did not extract any carbon from the B_{22}hir horizon.

Saugatuck-AuGres: The more acidic extractants (Na_2-NTA and Na_2-EDTA) were more efficient in extraction of organic carbon from the lower B horizons, such as B_{22}hir,

IIB_2hir', and IIBhir'm. However, the upper B ($B_{21}hir$) gave higher recoveries with the high pH Na_5-DPTA extractant. In general, from 21% to 71% of the total organic carbon was extracted by the four chelating agents used in the study.

AuGres-Croswell: The low pH extractants (NTA, EDTA) removed more carbon than the high pH extractants from the $B_{21}hir$ horizon of this soil series. In the better drained Croswell-Graycalm high pH solutions (pP_{04}, DPTA) were unable to extract detectable quantities of carbon.

Hiawatha $B_{21}hir$ and Munising $B_{21}hir$ resulted in the highest percentage of total carbon extracted by all the extractants used. However, the $B_{22}ir$ horizons of these soils contain somewhat less extractable carbon. Comparing these data with those of surface horizons of the same soils, it appears that these extractants are much more specific to the forms of organic matter eluviated from the upper part of the soils.

The Onaway $B_{21}ir$ horizon was also extracted efficiently by the extractants, although lesser amounts of carbon were removed. In general, the low pH extractants appear to be somewhat more efficient in extracting the illuvial carbon.

Statistical analyses: The data were statistically analyzed using a Control Data Corporation (CDC) 3600 digital computer. The Michigan State Agricultural experiment

station STAT routines were used. The extractable Fe, Al and C by different extractants were subjected to analysis of variance. The two-way analysis of variance with interaction was used for Fe and Al. The categories were soil horizons and extractant. The design used for carbon was the same except for the use of the method of fitted constants to account for the highly unbalanced data. Analysis of the variance of the data is shown in Table 12. The F test shows that the differences due to soils and extractants are highly significant at the 1% level. However, the statistical analysis failed to show a significant difference for carbon due to different extractants at the 1% and 5% levels.

The Tukey's W-procedure was used to compare the treatment means. The following conclusions are drawn from the computation of the data.

The results for Fe extraction reveal that there was a significant difference between the extracting power of the NTA, pyrophosphate, and EDTA extractants at the 5% level. The treatment means are ranked in an increasing order and the results of the Tukey's test for Fe with least significant range (LSR) (5%)=.0265 can be summarized as follows:

NTA	pPO_4	EDTA
.1673	.1383	.0973

The three means are significantly different.

Table 12. Analysis of variance of the extractable Fe, Al and carbon

	Fe		Al		C	
Source of variance	d.f.	M.S.	d.f.	M.S.	d.f.	M.S.
Soils	29	0.1107**	29	0.1705**	23	0.1888**
Extractant	2	0.0742**	3	0.0990**	3	0.0082 NS
Soil extractant	58	0.0036	87	0.0053	45(1)	0.0398
Remaining error	90	0.0004	120	0.0006	72	0.0009
Total	179		239		143	

** = highly significant at 1% level
NS = not significant at the 5% level

(1)= degree of freedom for interaction reduced owing to missing treatment combinations.

The Tukey's test for Al with LSR (5%)=.0348 is summarized below:

DPTA	NTA	pPO_4	EDTA
.2407	.2117	.1780	.1470

(any two means not underscored by the same line are significantly different.) The results show that although the NTA and DPTA extractants result in higher extraction of Al, the differences between them are not significant at the 5% level. However, the DPTA results are significantly different from the pyrophosphate extraction results. The latter is also not significantly different from the EDTA results. The differences between NTA and pPO_4 is approaching significance at the 5% level.

A modified Tukey"s LSR (5%) was used for comparison of the carbon treatment means due to unbalanced number of observations in each treatment mean. Generally Tukey's LSR is defined by equation

$$W = q_{\alpha}(P, n)\, S\bar{x}$$

W = LSR

$q_{\alpha}(P, n)$ is a factor obtained from a table of upper percentage points of the studentized range with p treatment, n error degree of freedom and an α error rate.

$S\bar{x}$ = standard error of the mean

In the case of unequal observations on each mean a modification is suggested by Sokal and Rohlf (1969) as:

$$S\bar{x} = \sqrt{s^2 \quad \frac{n_1 + n_2}{2n_1n_2}}$$

where s^2 = variance of individuals

n_1 = number observed on the first mean in the comparison

n_2 = number observed on the second mean in the comparison.

The two low pH extractants demonstrated the greatest efficiency in extraction of carbon. The differences between them are significant at the 5% level. The EDTA extractant results are also significantly different from the high pH pyrophosphate and DPTA extractants, while the NTA is not. The Tukey's test for carbon extraction can be summarized as follows:

EDTA	NTA	pPO_4	DPTA
.5117	.3717	.3417	.2917

(any two means not underscored by the same line are significantly different.)

The above statistical analysis reveals that DPTA extracted the highest amounts of Al, and EDTA the highest amounts of carbon from the spodic horizons used in this study. However, the former is not a suitable extractant for Fe due to its high pH, and the latter extracted the lowest

amounts of Fe and Al from the soils used. Therefore, the extractant which resulted in the most effective extraction of Fe, Al, and carbon from the spodic horizons used was the low pH, .1M Na_2-NTA.

Classification of the soils: The pedons used in this study are classified according to the criteria explained in the new soil classification system (Soil Taxonomy, 1970, uned.) and as given by Collins (1971) and Lietzke (1968), as follows:

(1) Kinross (organic surface): Histic Haplaquod; sandy, mixed, frigid.

(2) Saugatuck-AuGres: Aeric Haplaquod; sandy, mixed, frigid, ortstein.

(3) AuGres-Croswell: Entic Sideraquod; sandy, mixed, frigid.

(4) Croswell-Graycalm: Entic Haplorthod; sandy, mixed, frigid.

(5) Omega: Typic Udipsamment; mixed, frigid.

(6) Eastport: Spodic Udipsamment; mixed, frigid.

(7) Rubicon: Entic Haplorthod; sandy, mixed, frigid.

(8) Hiawatha: Typic Haplorthod; sandy, mixed, frigid.

(9) Onaway: Alfic Haplorthod; fine-loamy, mixed, frigid.

(10) Munising: Alfic Fragiorthod; coarse-loamy, mixed, frigid.

The chemical criteria for classification of Spodosols considered in this study are the accumulation index and the ratio of % pyrophosphate extractable Fe and Al to % clay,

Table 13. The index of accumulation is expressed as [CEC(pH 8.2) - 1/2% clay] times [thickness in cm.] = 65. This index is a measure of the amount of amorphous material in the spodic horizon. The calculation of the index is based on the consideration of the high cation exchange capacity of the amorphous material, as well as the % clay and thickness of the horizon. This would set some lower limit for the amount of precipitated illuvial material. The % clay is considered in an attempt to correct for that part of the exchange capacity which is a function of the silicate clay present in the soil. The reason for the consideration of the soil horizon thickness is to evaluate the vertical distribution of the amorphous material in the spodic horizon.

The criterion of the % pyrophosphate extractable Fe and Al over % clay being equal or greater than .2, in some sub-horizon, is based on the fact that the extraction with pyrophosphate at pH=10 is selective for the compounds that are typical of spodic horizons. Furthermore, since small amounts of sesquioxides are associated with clay surfaces or other amorphous materials present in the soil, the % clay is considered to allow for the adsorbed iron and aluminum oxides.

Table 13 shows the above ratios and the Fe and Al/% clay ratios with other chelating agents substituted for pyrophosphate. The spodic horizons studied generally agree

with the required accumulation index. However, the exceptions are Omega and Eastport.

Most of the soils do not meet the required ratio of % extractable Fe and Al/% clay. This is particularly true with the highly expressed spodic horizons in the field, such as Munising. In general, EDTA extraction has resulted in a lower Fe + Al/% clay ratio as compared with the other extractants. The NTA, pPO_4 and DPTA ratios are fairly comparable.

The changes of the % Fe + Al to % clay within the profile can be further summarized as follows:

(1) In two of the soil profiles, namely Saugatuck-AuGres and Hiawatha, the ratio of Fe + Al/% clay increased with depth. The higher ratios were observed in the lower spodic sub-horizons.

(2) In AuGres-Croswell the higher ratio of Fe + Al/% clay occurred in the upper spodic B horizon.

(3) In Kinross, Onaway, and Munising, the Fe + Al to % clay remained constant throughout the profile.

(4) In Croswell-Graycalm the ratio of Fe + Al/% clay increased to a certain depth (lower B_{21}hir). Beyond that depth the ratio decreased.

(5) Rubicon showed a decrease of the ratio with depth with EDTA and pyrophosphate extraction. However, the NTA and DPTA extractions resulted in a constant ratio throughout the profile.

Table 13. The accumulation index and the percent extractable Fe plus Al over % clay by different extractants of spodic horizons used in this study

Soil Series	Horizon	Acc. index	Extractant and % Fe + % Al/% clay			
			NTA	EDTA	pPO_4	DPTA
Kinross	$B_{21}h$	181.4	.05	.05	.04	.02
	$B_{22}hir$	79.6	.04	.03	.05	.02
Saugatuck-AuGres	$B_{21}hir$	65.3	.08	.05	.07	.08
	$B_{22}hir$	109.1	.06	.05	.05	.07
	$IIB_{21}hir'$	227.1	.13	.11	.11	.16
	IIBhir'm	135.1	.15	.15	.20	.17
AuGres-Croswell	$B_{21}hir$	64.7	.14	.07	.12	.13
	$B_{22}hir$	44.8	.08	.03	.06	.08
Croswell-Graycalm	$UppB_{21}hir$	6.0	.08	.04	.06	.08
	low $B_{21}hir$	32.5	.11	.08	.10	.11
	$B_{22}hir$	45.5	.07	.03	.06	.11
Omega	B_{22}	19.3	.11	.02	.05	.11
Eastport	B_{21}	28.2	.17	.10	.18	.30
Rubicon	$B_{21}ir$	82.8	.17	.08	.11	.16
	A1	64.9	.02	.01	.02	.004
	$B_{22}ir$	27.3	.16	.03	.07	.16
	ortstein	-	.33	.17	.28	.35
Hiawatha	A1	78.5	.02	.01	.01	.002
	$B_{21}hir$	97.5	.12	.10	.11	.11
	$B_{22}ir$	172.9	.32	.15	.28	.27
Onaway	$B_{21}ir$	65.5	.04	.02	.04	.05
	$B_{22}ir$	34.6	.03	.02	.03	.05
	$B'_{22}t$	46.0	.02	.01	.01	.01
Munising	A1	61.3	.02	.02	.02	.002
	$B_{21}hir$	209.2	.09	.10	.10	.09
	$B_{22}ir$	221.4	.11	.08	.10	.11
	$B_{3}x$	20.8	.03	.02	.03	.01

From the consideration of the above criteria, it is highly desirable to set a limit for the ratio of Fe & Al/ % clay to prevent the exclusion of the well-developed spodic horizons observable in the field. This is particularly true for those with a low extractable Fe and Al content or high percentage of clay, which tend to lower the ratio below the currently accepted required value. It is suggested to lower the ratio of Fe & Al/ % clay to = 0.10 to include most Spodosols (AuGres-Croswell, Croswell-Graycalm, and Munising). The same ratio is suggested to be set at = .04 for the well-drained, fine-textured Spodosols as well as the poorly-drained Spodosols (Onaway and Kinross series).

The older chemical criteria for spodic horizons calls for the ratio of % total carbon or % extractable carbon, % extractable Fe, and % extractable Al over % clay. Different extractants were used for Fe and Al extraction. Consequently, different limits were proposed (Lietzke, 1968). Such ratios were set at = .12 when total carbon and acid ammonium oxalate was used. Table 14 shows the ratio of % total carbon plus % extractable Fe and Al over % clay with the extractants used in this study. The available oxalate extractable Fe and Al of Lietzke is also included for comparison. All of the spodic horizons used in the study meet the required ratio in some sub-horizon. Since carbon is one of the main constituents of the illuvial material of the

spodic horizon in these soils, it is suggested that the ratio be used in preference to the % Fe & Al/ % clay ratio currently in use.

Table 14. The ratio of % total C, % extractable Fe, and % extractable Al over % clay for spodic horizons used in the study

Soil Series	Horizon	Extractant and % C + % Fe + % Al / % clay				
		NTA	EDTA	pPO_4	DPTA	Oxalate
Kinross	$B_{21}h$	.58	.58	.57	.55	-
	$B_{22}hir$	.40	.39	.41	.38	-
Saugatuck-AuGres	$B_{21}hir$	.33	.30	.32	.33	-
	$B_{22}hir$	.28	.27	.27	.29	-
	$IIB_{21}hir'$	.60	.58	.58	.63	-
	IIBhir'm	.77	.77	.82	.79	-
AuGres-Croswell	$B_{21}hir$	.44	.37	.42	.43	-
	$B_{22}hir$	.20	.15	.18	.20	-
Croswell-Graycalm	Upp.$B_{21}hir$	.19	.15	.17	.19	-
	low $B_{21}hir$	.35	.32	.34	.35	-
	$B_{22}hir$	.16	.12	.15	.20	-
Omega	B_{22}	.26	.17	.20	.26	.25
Eastport	B_{21}	.38	.31	.39	.51	.37
Rubicon	$B_{21}ir$	.45	.36	.39	.44	.40
	$B_{22}ir$	.31	.18	.22	.31	.29
	ortstein	1.01	.85	.96	1.03	1.08
Hiawatha	A_2	.40	.38	.39	.36	-
	$B_{21}hir$	.43	.41	.42	.42	.44
	$B_{22}ir$	.92	.75	.88	.87	.78
Onaway	A_2	.30	.30	.31	.29	-
	$B_{21}ir$	.13	.11	.13	.14	.15
	$B_{22}ir$	.10	.09	.10	.12	.13
	$B_{22}t$	.07	.06	.06	.06	-
Munising	A_2	3.8	3.7	3.7	3.3	-
	$B_{21}hir$	.39	.40	.40	.39	.40
	$B_{22}ir$	.35	.32	.34	.35	.33
	B_3x	.13	.12	.13	.11	-

SUMMARY AND CONCLUSIONS

This research was initiated to study the degree of accumulation of the illuvial material, as measured by different extracting media and influenced by pedological processes and soil formation factors, in the B horizons of Spodosols. The illuvial material of interest (active material) is considered to be composed of sesquioxides (particularly those of Fe and Al) and organic matter. The following conclusions may be drawn from the discussion of the results.

Soil drainage and the illuvial material: The negligible quantities of extractable Fe in the extracts of poorly-drained Kinross soil may be explained by considering the following possibilities: (1) Since the water table is very close to the surface and it commonly averages 6 inches below the surface during the growing season, it is unlikely that the precipitation of iron oxides have occurred by occasional flushes of oxygenated water which oxidize ferrous compounds and decrease their solubility. However, the possibility of microbial oxidation should also be considered. (2) The presence of the prevailing reducing conditions probably have resulted in the occurence of the iron in the reduced (Fe^{++}) form. Consequently it could have been leached away from the sub-soil, since that is the more soluble form

of iron. This phenomenon can be supported by Deb's (1949) study in which the author concludes that the low pH of most podzols precludes the existence of any iron as Fe^{++}, which is soluble at those reactions.

The data obtained in this study shows the amounts of extractable Fe from the poorly drained Kinross subsoil is negligible, even when the low pH extractants were used. Therefore it invalidates the possibility of the existence of the oxidized Fe. Furthermore, it is suggested that Al may be assigned a major role in stabilizing the organic matter in the B horizons of this soil, although the quantities of extractable Al are also low in the subsoil of Kinross.

The better-drained soils of this drainage catena are shown to have a higher amount of extractable Fe. The imperfectly-drained Saugatuck-AuGres contains more extractable Fe in the upper B horizon, and decreasing amounts in the lower B horizon, where the lower part of this horizon occurs at the average observed depth to the water table. The AuGres-Croswell maximum extractable Fe occurs in the upper B horizon, while Croswell-Graycalm has its maximum Fe accumulation in the lower B horizon. The maximum extractable Fe of the latter two soils correlate with the maximum extractable organic matter, suggesting greater complex formation in those horizons. Among the soils of this toposequence, AuGres-Croswell has exhibited the highest extractable Fe. However,

this is not in agreement with the greatest extractability of organic matter in the toposequence, and consequently the highest intensity of spodic horizon development, as will be seen later in this chapter.

The magnitude of the Al extracted by all of the chelating agents equals or exceeds the corresponding amounts of iron extracted from the spodic horizons in all the soils studied except Eastport, Hiawatha $B_{22}hir$, and Onaway. This may be a reflection of the greater involvement of Al in chelation reactions with organic matter, or the excess of the total Al over Fe present in the soil. The latter possibility may be more valid since the exchangeable Al equals or exceeds, the total citrate-dithionite extractable Fe, except in the Eastport and Onaway pedons. In the poorly-drained Kinross soil it is definitely shown that Al is the major element associated with the extractable organic matter. However, it is difficult to say which metal has the predominant influence in combining with the organic fraction of the spodic horizons of the other soils.

The amounts of Al do not seem to be influenced by drainage as much as Fe. However, the poorly-drained Kinross soil contains the lowest amount of extractable Al while the somewhat poorly drained Saugatuck-AuGres has the highest extractable Al, with two maxima, the second maxima being associated with a different parent material, IIB_2. The high

content of Al in Saugatuck-AuGres correlates with the high accumulation of organic matter as well as the intensity of spodic horizon development in this soil.

It is apparent from the extraction data that considerable amounts of the B horizon organic matter are associated with a fraction of the total sesquioxides. Furthermore, it is evident that the chelating extractants are specific to the extraction of the organic matter present in the B horizons, since very small amounts of carbon were extracted from the surface A horizon.

Spodosols of various degrees of spodic horizon development and the illuvial material: The amount of complexed iron increases from the weakest spodic horizon expression to the strongest development. The maximum extractable Fe occurs in the upper B horizon in all the soils of this group. The Omega and Eastport, which are classified as Typic Udipsamments (Brown Podzolic soil) and Spodic Udipsamment (Regosol Podzol intergrade), respectively, contain the lowest amounts of extractable Fe. Other more developed spodosols, such as Rubicon, Hiawatha, and Munising series, contain higher amounts of extractable Fe.

The amounts of extractable Al show the same trend as Fe, in which it increases with the intensity of pedological development. The Al and Fe maxima occur in the same horizon ($B_{21}ir$) in Rubicon and Onaway soil series, while this is

not the case with Hiawatha and Munising. In the latter the maximum Al occurs deeper in the profile, namely in the lower spodic B horizon ($B_{22}ir$). Extractable Fe is considerably predominant in the Onaway and Munising profiles, while Al is predominant in the Rubicon and Hiawatha profiles. However, Hiawatha $B_{21}hir$ has more extractable Fe compared to Al.

A high percentage of extractable carbon, as calculated from the difference between the non-extracted and extracted soils, occurs in the spodic horizons. This is especially true in subsoils with a high initial carbon content. The extractable C maximum occurs at the same horizon ($B_{21}ir$) of Fe and Al maxima in Rubicon and Onaway series. However, Hiawatha and Munishing extractable C and Fe maxima occur at the upper B horizon ($B_{21}hir$) while the Al maximum occurs at the lower $B_{22}ir$ horizon. This may suggest the predominant role of Fe in these soils in the solubility of organic matter.

Statistical analyses: The statistical analysis of the extraction data reveals that the NTA, pPO_4, and EDTA extraction procedures for Fe produce results with significant differences between them. The extractable Fe, EDTA values are significantly lower than the other extractants. The NTA extractable Fe is indicated to be a good estimate of the amount of complexed Fe.

The DPTA and NTA extractable Al are also comparable. However, NTA and pPO_4 extractable Al are not significantly different from each other, while DPTA extractable Al results are significantly higher than pyrophosphate and EDTA results. Therefore NTA is suggested to be a suitable extractant for Al.

The extraction of carbon has been more successful with the low pH solutions. EDTA and NTA extractable carbon are significantly different from each other. However, EDTA is significantly different from the other two high pH extractants, while the NTA resulted in comparable amounts of extractable C with the high pH extractants. Even though EDTA has the highest efficiency for the extraction of carbon, it resulted in the lowest extractable Fe and Al. Therefore, the overall statistical analysis suggests that the low pH, .1M NTA solution is the most suitable extractant for Fe, Al, and C from the Michigan spodic horizons.

Chemical criteria in soil classification: The chemical criterion of the % extractable Fe and Al over % clay, for the classification of Spodosols, is suggested to be lowered to = 0.10 to include most Spodosols (AuGres-Croswell, Croswell-Graycalm, and Munising). It is also suggested that the required ratio needs to be lowered to = 0.04 for the well-drained, fine-textured as well as the poorly-drained Spodosols (Onaway and Kinross series). The data obtained in

this research also indicate that the % total carbon, % extractable Fe, and % extractable Al over % clay, = .12, the previous criterion for classification of Spodosols, gives a much better estimate of the active illuvial material of the spodic B horizon. Therefore it is suggested that this ratio be used in preference to the currently used ratio of % extractable Fe and Al over % clay.

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