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LOW MOLECULAR WEIGHT PHENOLIC COMPOUNDS
IN
HYDROSEQUENCES AND DEVELOPMENTAL SEQUENCES
OF MICHIGAN SPODOSOLS
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GEORGE FLOYD VANCE

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LOW MOLECULAR WEIGHT PHENOLIC COMPOUNDS
IN
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By

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ABSTRACT

LOW MOLECULAR WEIGHT PHENOLIC COMPOUNDS IN HYDROSEQUENCES AND DEVELOPMENTAL SEQUENCES OF MICHIGAN SPODOSOLS

By

George Floyd Vance

Spodosol hydrosequences and developmental sequences were studied to 1) test chemical classification criteria and 2) determine the phenolic compound distribution within pedons. A new chemical criteria placed the ten pedons into soil orders respective of their morphological characteristics, whereas Soil Taxonomy and Canadian classification systems placed only 5 and 7, respectively. Low molecular weight phenolic compounds were analysed using high pressure liquid chromatography. Three benzoic acids - protocatechuic, *p*-hydroxybenzoic, and vanillic acids, two aldehydes - vanillin and *p*-hydroxybenzaldehyde, and two cinnamic acids - ferulic and *p*-coumaric acids were identified. The benzoic acids accounted for the greatest portion of phenolic compounds in each horizon. Protocatechuic acid dominated the spodic horizons while *p*-hydroxybenzoic and vanillic acids were highest in the A horizons. Concentrations of protocatechuic acid, iron and aluminum were greater as depth to water table decreased and as spodic horizon expression increased. Protocatechuic acid with its ability to form chelate complexes with iron and aluminum and its prevalence in spodic horizons suggests it may play an important role in the formation of Spodosols.

ACKNOWLEDGEMENTS

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Introduction

Spodosols are soils which have accumulated amorphous forms of illuvial organic matter, aluminum, and frequently iron in their B horizons. Although spodic horizons are generally very distinctive when viewed in the context of an entire profile in the field, minimally developed horizons often require laboratory analysis to determine if sufficient accumulations are present to fulfill spodic horizon criteria.

Spodic horizon genesis is believed to involve formation of soluble organo-metallic complexes from the interaction of low molecular weight organic compounds and sesquioxides (oxides of aluminum and iron). In aqueous environments, organic acids with carboxylic and phenolic hydroxyl functional groups can become ionized through proton dissociation, which increases the potential for interacting with metal ions. The term "cheluviation" was suggested by Swindale and Jackson (1956) to describe the process by which soluble organo-metallic complexes form through mineral decomposition by chelation and subsequent eluviation of the complex. The complexes form in eluvial horizons (A and E), are translocated downward, and are ultimately either immobilized in the B horizons or leached completely through the soil profile into ground waters.

Although several studies have implicated different mechanisns by which spodic horizons form, organic acids involved have received little attention. Therefore, the objectives of this study are:

1) to characterize and classify the soils of hydrosequences and developmental sequences of Spodosols by chemical criteria of Soil Taxonomy, Canadian System of Soil Classification, and a set of new chemical criteria (Mokma, 1983);

2) to evaluate sodium hydroxide and sodium pyrophosphate at pH 7 and pH 10 to determine their efficiency in extracting low molecular weight phenolic compounds of a possible pedogenic nature; and
3) to determine the concentrations of phenolic compounds in each horizon of the soils within the hydrosequences and developmental sequences of the Spodosols studied and to interpret their relative importance in the podzolization process.

CHAPTER 1

LITERATURE REVIEW

LITERATURE REVIEW

The Spodosol order was introduced with the development of the new comprehensive soil classification system, Soil Taxonomy (Soil Survey Staff, 1975). The concept of the Spodosol evolved primarily from that of the earlier Podzol definition. Soil classification systems from other countries usually maintain the Podzol name. Therefore, the terms, Podzol and Spodosol, are both used throughout this review with the understanding that each are similar in concept.

I. SPODOSOL CONCEPT

Historical Development of the Spodosol Concept

The concept of Podzols was originally developed in Nineteenth Century Russian soil studies, which recognized an ashy gray to white eluvial horizon at or near the soil surface (Muir, 1961; Petersen, 1976). It was nearly 150 years ago that Sprengel described a bleached soil layer, which he called BLEISAND (Joffe, 1931; Muir, 1961). In 1862, a German soil scientist, Senft, was one of the first to recognize ortstein or ortsand occurrences below the bleached horizon (Muir, 1961). Although a connection between the bleached horizon and the ortstein was made, the bleached material continued to have priority in soil formation studies. Dokuckaev and co-workers in the late 1800's repeatedly examined Podzols in order to determine their origin (Ponomareva, 1964). However, it was not until 1888 that Muller and Georgievskii independently pointed out the genetic relationship between the eluvial bleached horizon and the underlying illuvial horizon (Muir, 1961; Ponomareva, 1964).

The concept of Podzols was introduced into the United States through the German school, which defined a Podzol as being bleisand with an associated underlying layer of ortstein (Muir, 1961). Lectures by Marbut and his translation in 1928 of the work by Glinka brought out Podzol concepts that emphasized German and Russian philosophies (Joffe, 1931; Muir, 1961).

In the 1938 system of soil classification in the United States several soils were classified as Podzolic or Podzols (Baldwin, 1938). The Gray-Brown Podzolic and Red-Yellow Podzolic groups were characterized by translocated sesquioxides and/or humus. In 1960 the new U.S. soil classification system was introduced. The Podzolic and Podzol classifications were eliminated. These soils were separated into orders that emphasized either clay translocation or translocation of sesquioxides and/or humus. The new Spodosol order was developed to include soils that had a "spodic" horizon which was defined as an illuvial horizon of translocated humus and aluminum with or without iron (Soil Survey Staff, 1960). Soils witha bleached eluvial horizon are classified according to their illuvial horizon.

Environmental Setting of Northern Spodosols

The formation of a Spodosol is dependent on the five soil forming factors: parent material, climate, organisms, topography, and time. They are found primarily in areas of cool humid or prehumid climates but have also been reported in warm, humid tropical (Klinge, 1965; Soil Survey Staff, 1975) and warm, dry summer, mountainous regions (Tan et al., 1970). The soil forming factors will be briefly described for only the northern cool regions because Spodosols are of the greatest extent here and play an important role in the utilization of the land.

PARENT MATERIAL: Spodosols occur mainly in late Pleistocene or Holocene coarse-textured glacial deposits of sandy outwash plains, gr

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CLIMATE: Areas of cool climates and soil temperature regimes of the frigid and cryic classes are the major environments in which Spodosols are found (Soil Survey Staff, 1975).

ORGANISMS: Spodosols are dominate by coniferous or mixed hardwood vegetation and predominately fungi microorganisms.

TOPOGRAPHY: Spodosols occur on level to steeply sloping surfaces with aquic or udic moisture regimes (Soil Survey Staff, 1975).

TIME: Under optimum conditions only a few hundred years are required to form a spodic horizon (Soil Survey Staff, 1975) although 8000 years were needed for a well-developed Spodosol in Michigan (Franzmeier and Whiteside, 1963).

Morphological Characteristics of Spodosol Profiles

Spodosols are generally easily recognized in the field. A profile that represents Spodosol morphology has distinct horizonation. The A horizon is dark colored, indicating the accumulation of organic materials. Below the dark surface horizon is a light colored E horizon indicating eluviation has taken place. The color of this horizon is due primarily to uncoated sand and silt particles. Below the eluvial horizon is an illuvial layer, the spodic horizon. The spodic horizon is red to dark brown in color, signifying that products of translocated iron, aluminum, and organic matter have accumulated. The parent material or C horizon occurs below the spodic horizon and it is generally yellowish in color. Such profiles are found in coarse-textured materials, usually in areas forested with coniferous or mixed hardwood species.

The presence of certain soil properties that are identifiable in the field can be sufficient to classify a soil as a Spodosol. Ortstein that is continuously cemented for a thickness of at least 2.5 cm is classified as a spodic horizon. Other subhorizons that have either sandy or coarse-loamy particle size classes and has recognizable cracked coatings on the grains and/or dark coarse-silt sized pellets are also diagnostic field identifiable properties of the spodic horizon (Soil Survey Staff, 1975).

II. SPODOSOL GENESIS

Podzolization

Podzolization involves the overall reactions and processes that result in the mobilization, translocation, and immobilization of organic matter, aluminum, and iron. A series of events occurs during podzolization which includes processes of addition, loss, migration, and transformation. From the inception of podzolization, the series of events may proceed in the following manner:

1) Organic matter accumulates on the surface of the soil and decomposes releasing organic compounds which are acidic and reactive. Products of decomposition may include fats, waxes, and resins which are fairly resistant to early degradation and therefore allow humus to build (Ponomareva, 1964).
2) Carbon dioxide forms from oxidation of organic matter and respiration of microflora and microfauna. Carbon dioxide reacts with water to form carbonic acid. Organic and inorganic acids acidify the surface horizon while also weathering soil minerals (Schnitzer and Kodama, 1977; Stevenson, 1982).
3) Soluble acids dissolve carbonate minerals and the dissolved

products move with the percolating waters. A pH gradient is established. Replacement of exchange cations (Ca, Mg, Na, K) by hydrogen and aluminum takes place (Boul et al., 1973).

4) When soil pH has dropped below pH 5, ferromagnesium minerals illite and chlorite, and feldspars weather, releasing Fe, Al, Mg, and K into the soil solution (Franzmeier and Whiteside, 1963).
5) Fulvic acids and ploγphenols form complexes with the released Fe and Al and migrate until immobilization and/or precipitation occurs.
6) Immobilization results when the organo-metallic complex becomes saturated with additional cations or when changes in ionic concentration or pH occur (DeConinck, 1980).

Over time there forms a well-developed profile which shows the morphological features previously described and would be classified as a Spodosol.

Succeeding sections will review vegetational and microbiological organic products and their interaction with iron and aluminum (sesquioxides) and also the chemistry of Spodosols with particular reference to the organic compounds.

Vegetation

The compounds that occur in aqueous leaf extracts and forest canopy leachates and which have a superior role in the interactions with iron and aluminum are various organic acids which contain both hydroxyl and carboxyl functional groups. These water-soluble organic compounds are also known to act as growth inhibiting substances (Rice, 1974; Blaschke, 1979). Therefore, not only do these organic acids play a major role in

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the podzolization process but they may also control the destiny of the forest composition thus influencing podzolization indirectly.

Plant materials contain various kinds and amounts of organic constituents that are classified into six main categories: 1) cellulose (comprising 15-60% of the plant), 2) hemicellulose (10-30%), 3) lignin (5-30%), 4) water soluble fraction which includes simple sugars, amino acids, and aliphatic acids (5-30%), 5) ether or alcohol soluble fraction which includes fats, oils, waxes, resins, and pigments, and 6) proteins. As plants age the percentage of water soluble and protein fractions decreases (Alexander, 1977).

The contents of polyphenols, waxes, resins, and lignin in leaves have been related to decomposition rates whereas the ultimate formation of mull or mor humus layers was more dependent on bases, aluminum, and carbon/nitrogen levels (King and Heath, 1967; Millar, 1974; Messenger, 1975). Leaf decomposition studies have demonstrated that rapid decreases in sugars and polyphenols occur shortly after leaf fall (Hayes, 1965; Anderson, 1973). Dormarr (1970) found seasonal patterns in the concentration and variety of water soluble substances occurring in poplar leaves. The poplar leaves contained low molecular weight phenolic compounds early in the season while more complex phenolic compounds occurred later in the season. There were increased losses of phenolic substances late in the growing season, during senescense and after leaf fall.

Organic substances released during plant decomposition or from forest canopy leachates are thought by many to play an important role in the mobilization of metal ions (Schnitzer and DeLong, 1955; Coulson et al., 1960; Muir et al., 1964). The presence of these organic

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substances and their effects on the podzolization process varied greatly with different tree species (Andersen, 1979; Johnson and Siccama, 1979; Herbauts and DeBuyl, 1981).

Herbauts and DeBuyl (1981) found incipient podzolization under an 80 year old spruce stand but found no evidence of podzolization in the surrounding climatic beechwood forest. Development of a mor humus layer in the spruce stand was believed to accentuate the processes of podzolization. Organic acids are shown to migrate deeper in the soil profile under the influence of the spruce vegetation. Changes over time in the vegetation and the formation of a mor humus layer were shown to produce a soil with a spodic horizon from an Inceptisol having only an A and C horizon solum (Andersen, 1979). The changes occurred in approximately 250 years.

Profile development can vary under a single tree canopy, Crampton (1982) related this variation to incoming organic substances and the canopy leachate pattern. He found more stemflow in broadleaf species and less in coniferous species. Lower acidity levels were shown in the stemflow of conifers and also where soils became drier. It was hypothesized that lower soil leaching and higher acidity of the incoming solutions caused greater podzolization under conifers and especially closer to the tree stem.

Johnson and Siccama (1979) investigated the effect of hemlock, white pine, and American beech on the morphology of the soils beneath them. The age of the trees ranged from 50-200 years for the hemlock and pine and 150-200 years for the beech. Under hemlock, humus layers were lower in pH and the E and Bhs horizons showed greater soil morphological development. The soil under pine showed the highest pH in the humus layer and the least soil development. Canopy leachate solutions indicated the hemlocks have a greater capacity to absorb iron before precipitating. The greater acidity in the humus layer and the higher capacity to absorb iron influenced the morphology of the soils more so under hemlocks than under beech or pine.

Bloomfield (1953a,b; 1954a,b,c) in a series of papers entitled "A Study of Podzolization" tested leaves of scots pine, kauri, rimu, larch, aspen, and ash for their ability to solubilize iron and aluminum. Under aerobic conditions he found that the reduction of ferric iron accompanied the dissolution of iron, which was believed to be due to the action of the organic substances in the leaf extracts. Ferrous iron and aluminum interacted with organic constituents to form coordination complexes. It was also noted that over time the ferrous-organic complex was oxidized to a ferric-organic complex. It is interesting to note from the study with scots pine needles that although oxidation increased as pH was raised, the ferric-organic complex formed at pH 7 had greater solubility than those forming at pH 4. Studies with the other species showed less solubility at higher pHs. It was also shown that non-microbiological processes were involved in bringing iron and aluminum into solution from ferric and aluminum oxides as this study was also conducted in the presence of toluene and chloroform.

Aqueous extractable substances from conifer and deciduous vegetation were found capable of interacting with iron and aluminum (Bloomfield, 1954c; Himes et al., 1963). The relative importance of the complexes formed were believed to be influenced by other variables resulting from leaf decomposition. While the leaves from coniferous species were low in bases and the deciduous usually high, the soils developed under them were acid and neutral, respectively. Bloomfield suggested the low translocation of organo-metallic complexes under deciduous species was caused by saturation of the organic compounds with bases. This would precipitate the organic compounds before any soluble complex between metal ions and organic compounds could form.

Bloomfield (1957) presented evidence for the possible involvement of polyphenols as well as carboxylic acids in iron and aluminum mobilization. After the removal of the carboxylic acids by using an anion-exchange resin, he found that the remaining solution was much less effective in solubilizing ferric oxide. The carboxylic acids were recovered from the resin and tests indicated that they had an increased solubilizing efficiency over the non-acid solutions; but even the sum of the acid and non-acid fractions gave lower solubilization ability than that of the original leaf extract. It was concluded that an additional reducing agent, polyphenols, must be involved, and that a synergistic effect occurred in the presence of both.

After the suggested involvement of polyphenols in the podzolization process, attempts were made to isolate specific polyphenolic compounds. Coulson et al. (1960a) found epicatechin and D-catechin to be the major polyphenols in the leaves of different tree species. They then tested the ability of these two compounds to mobilize and transpost iron and aluminum in model soil columns under different pH conditions (Coulson et al., 1960; Davies et al., 1960). Under more acidic conditions the polyphenols increased iron mobilization, whereas, aluminum showed no effects to pH change. The decreased interaction with iron at higher pHs was suggested bo the due to a structural change in the polyphenol compounds. When interaction took place between the polyphenols and the ferric iron, a stable complex was formed and iron was reduced. The reaction mechanism was thought to involve organic free radicals that formed non-ionic complexes with iron.

King and Bloomfield (1966) found epicatechin and D-catechin in larch extracts but only D-catechin in scots pine extracts. Various other organic compounds were also isolated including sugars, amino acids, and phenolic acids. The polyphenols and phenolic acids isolated in the leaf extracts included D-catechin, epicatechin, gallocatechin, epigallocatechin, gallic acid, protocatechuic acid, vanillic acid and ellagic acid. They also tested the main groups of compounds that were isolated to determine the effect each had on ferric oxide dissolution. They found that no interactions occur between ferric oxide and sugars or the amino acids when each was tested separately but in a solution containing the two, considerable adsorption resulted. The cause of this observation was suggested to be related to the Maillard reaction, a condensation reaction between carbonyl and amino acid groups. Both the polyphenols and the phenolic acids were apparently able to dissolve ferric oxide, form complexes, and then be adsorbed onto any residual ferric oxide surface.

In order to simulate the effects of canopy leaching during rainfall, Malcolm and McCracken (1968) immersed leaves of southern red oak, live oak, and longleaf pine in water. The only polyphenol that could be identified was that of epicatechin which was present only in the oaks. Reducing sugars were also determined and found to possess similar properties as the acidic polysaccarides characterized in poplar leachates by Schnitzer and DeLong (1955). Although organic acids were not analyzed directly, it was suggested that they were of a higher

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concentration than polyphenols and reducing sugars combined. They conclude that canopy leachates would be an important source of mobile organic compounds capable of mobilizing iron and aluminum and percolating through the soil.

Bloomfield (1957, 1965) and Coulson et al. (1960b) postulated a causal relationship exists between podzolization and polyphenol concentration in leaves. They were also of the opinion that the polyphenols active in podzolization were derived mainly from the forest canopy leachates. Hingston (1962), while studying aqueous extracts of eleven eucalyptus species and seven Western Australian tree and shrub species, found no correlation between quantity of polyphenols and solubilization of iron oxides. Some evidence of activity was shown to be due to the low molecular weight carboxylic or hydroxy acids. King and Bloomfield (1968) determined that drying of picked beech and larch leaves affected the subsequent amounts of polyphenols extracted by aqueous solutions. Drying was found to also accentuate the activity of iron dissolving ability by the leaf extracts. This raised doubts as to the validity of Bloomfield's earlier work since several of the leaves in those studies were also dried. Again a correlation between polyphenols and leaf extract activity could not be established.

Schnitzer and DeLong (1955) identified glucose, galactose, xylose, and arabinose sugars and uronic acids in aqueous extracts of poplar leaves and in the poplar canopy leachates. They concluded that the principal components of the extracts had the characteristics of an acidic polysaccharide. No evidence was found for chelation complex formation between organic compounds and ferric iron; therefore, they suggested that peptization and protective colloidal formation was the primary function of the organic compounds. Along with the acidic polysaccharide observation a joint study using the same leaf extracts and leachates showed that the iron mobilizing capacity of these solutions can increase as solutions percolate through soils having pH gradients similar to that found in Spodosols (DeLong and Schnitzer, 1955). It should be pointed out that these conclusions were made from tests at pH 5.5 and 7.5 only. It is important to note the effect of pH and iron capacity, for immobilization would be subjected to the proportion of iron and aluminum to organic matter as well as pH and cation effects.

Water soluble polysaccharides and phenolic compounds were isolated from poplar leaf extracts by Dormarr (1970). Polysaccharides were unable to react with ferric oxides. This observation was also noted by Bloomfield (1958) with polysaccharides extracted from aspen leaves. When a column containing some ferric oxide was leached with the poplar leaf extract the phenolic compounds were retained. This was assumed to be equivalent to the ability of phenolic compounds to dissolve iron, but adsorption as well as dissolution may have also occurred. From this work one could conclude that phenolic acids are involved in the podzolization process, although polysaccharides may play an indirect role.

Muir et al. (1964a) found seventeen amino acids and four organic acids in the aqueous extracts of scots pine needles. The capacity of the amino acids to maintain iron in solution was low and diminished rapidly at pH levels greater than 4.5. Three of the four organic acids were active in maintaining iron in solution. These acids included citric, malic, and quinic which are α-hydroxyl carboxylic acids. Citric acid showed the greatest capacity to solubilize as well as mai

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maintain large amounts of iron in solution. Following DeLong and Schnitzer (1955) they noted that as pH increased, organic acids were able to maintain greater amounts of iron in solution, and that calcium reduced the solubility (Muir et al., 1964b).

Studying the effects of both high and low molecular weight substances from aqueous extracted maple and oak leaves Himes et al. (1963) found that increases in pH caused greater solubility of ferric hydroxide with the high than with the low molecular weight fraction. Electrophoresis showed the complexes formed were charged and that the reaction between iron and organic substances was due to phenolic constituent groups. Infrared spectroscopy indicated carboxyl groups were reacting with the iron as well.

Microorganisms and other soil animals

Microbial decomposition of tree leaves often starts as soon as the leaves form on the tree. Microorganisms on the leaf and in the soil litter layer play an important role in the release and/or formation of organic substances. Constituents of plant leaves can influence which microbial communities may be found in soil environments (Millar, 1974). The composition of the soil will also be affected by microbial growth regulating substances leached from vegetation or produced during plant decomposition, as well as microbial metabolites and the acidity of mor humus layers.

Coniferous litter usually forms a mor humus layer with pH levels generally below 4.5. In these humus layers earthworms are very rare, especially those of the *Lumbricus terrestris* species (Peterson, 1976). Mull humus layers have an abundance of these earthworms and coniferous litter is rapidly decomposed in this layer. The cellulase and chitinase

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enzymes produced to promote decomposition of the coniferous needles are either produced in the gut of the worm or by bacteria or protozoa present in the worm's gut (Millar, 1974). Enchytracid worms have been reported by Abrahamsen (Millar, 1974) to be very abundant in northern coniferous Podzols. These worms lack the enzymes necessary to decompose coniferous needles and plant materials pass through the worms with very little change.

Messenger et al. (1972) reported that soils with mor humus layers contained greater lengths of fungal hyphae and a lower number of bacteria and actinomycetes filaments than do mull humus layers. The lower average pH of 4.4 in the mor layer versus 5.2 in the mull layer could cause reduced bacteria and actinomycetes populations because they grow best at neutrality (Alexander, 1977). Actinomycetes are also known to decompose chitin, an intrigal polysaccharide of plants and microorganisms, especially the filamentous fungi (Alexander, 1977). This would explain why there are reduced numbers of fungal hyphae in the mull humus layers.

Messenger et al. (1972) also found that mor humus layers produced substantially greater amounts of organic acids than did mull layers. The higher organic acid content was suggested to be related to the fungi activity.

Fungi are the main decomposers of lignin but other groups possess lignin degraders as well. The white-rot fungi are considered to be the most active in lignin degradation. This group of fungi is found primarily in forest soils (Hurst and Burges, 1967).

Several phenolic substances are released during lignin decomposition, including p-hydroxybenzoic, protocatechuic, vanillic, syringic, p-hydroxycinnammic, and ferulic acids as well as their aldehydes (Flaig

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et al., 1975; Walker, 1975). These compounds are known to exist in plants and may also be derived through microbial synthesis. The isolation of many of these phenolic compounds in humus layers and canopy leachates leads one to believe their role in mobilizing iron and aluminum may be vital to the podzolization process.

Heath and King (1964) and Andersen (1973) suggested that an apparent inverse relationship exists between phenolic acid concentrations and the palatability of leaf litter to soil animals. Rates of leaf breakdown of different species were mainly due to the concentrations of gallic and protocatechuic acids (Heath and King, 1964). Although phenolic acids may contribute to the potential activity of the litter degrading microbes and soil animals, mean air and litter temperatures were also suggested as additional factors in controlling the degraders metabolism (Anderson, 1973).

A study by McKenzie et al. (1960) found that the biological activity in Spodosol profiles could influence the formation of spodic horizons. The distribution of citrate-oxidizing organisms in the upper horizons and the detection of iron-oxidizing organisms in the B horizons were suggested as the causal agents. They proposed as a possible mechanism of iron translocation being, first the reduction of iron takes place in the A horizon by the formation of complexes with di- and tricarboxylic acids, second the translocation of the complexes but since the citrate-oxidizing organisms also utilize the acids as an energy source, decomposition of the complex occurs, and last the reduced iron released from the complex is leached to the B horizon where it is immobilized as ferric iron by the iron-oxidizing organisms.

The activity of microorganisms and soil animals in Spodosols is as important as the forest tree composition, for together they form the organic substances needed for podzolization: the trees furnish the organic matter and the activity of the microorganisms and soil animals decompose it. Through the activity of microorganisms a number of acids are formed including fulvic, humic, carbonic, lichenic, nitric, sulfuric, and phosphoric acids (Barshad, 1964). These acids are capable of breaking down soil minerals which will liberate iron and aluminum, thus allowing their contribution to the podzolization process.

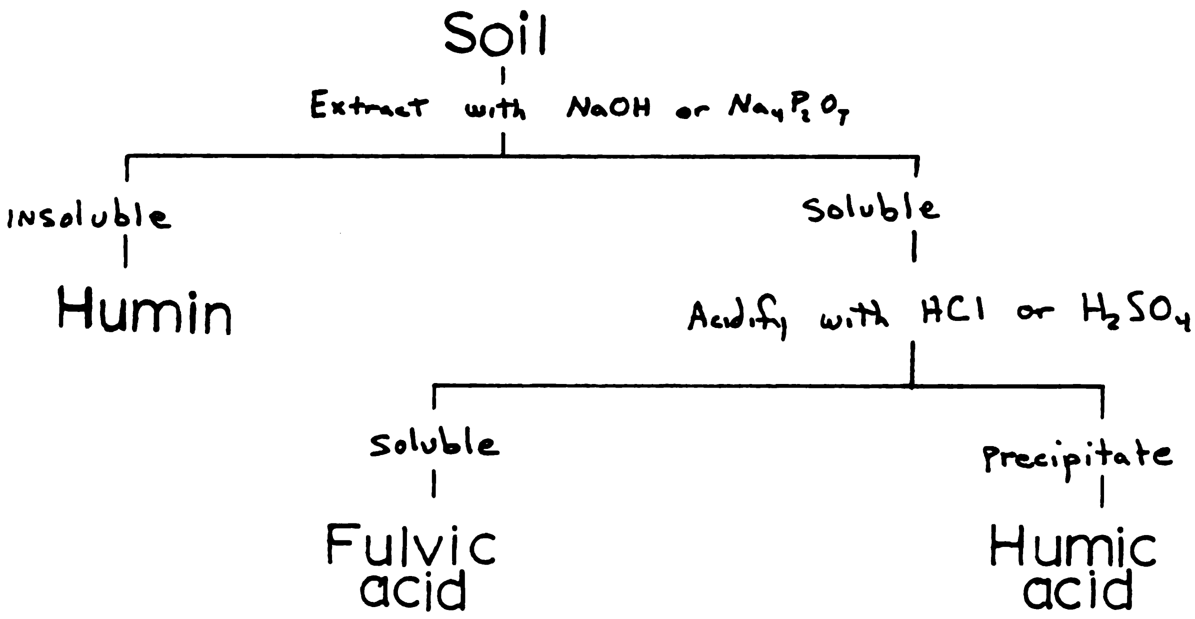
The role of microorganisms and soil animals is vital to the podzolization process. Alexander (1977) states that "Spodosols (are) of considerable interest to the microbiologist since the process (of formation) is associated with the decomposition of organic matter accumulated at the soil surface and with the downward movement of organic substances formed or released by the subterranean micro-inhabitants". Although the importance of microorganisms and soil animals is noted, there still exists a need for additional research into the role they actually play in the formation of Spodosols.

Spodosol Chemistry

The role of soil organic compounds that form soluble complexes with metal ions is important to the translocation of organometallic complexes in soils (Stevenson, 1983). Translocation and immobilization of these complexes are nowhere more evident than in the spodic horizons of a well developed Spodosol. Some of the organic compounds thought to be responsible for the initial solubilization have already been discussed previously. Those compounds were found either in surface horizons or canopy leachates. Therefore, this section will be primarily devoted to the characterization of organic substances extracted from within the

Spodosol profile.

Soil organic matter has been extracted from spodic horizons by numerous solvents. The classical method of extracting soil organic matter and that which is utilized in many studies is based on solubility differences at various pH levels. This technique fractionates soil organic matter into three broad categories: humin, humic acid, and fulvic acid. The procedure commonly used is as follows: 1) extract a soil sample for 24 hours with either 0.1-0.5 N sodium hydroxide or 0.1 M sodium pyrophosphate after displacement of extracting vessel gasses with nitrogen, 2) remove nonextractable materials by centrifugation and acidify the supernant with 2 N hydrochloric or sulfuric acid and let stand for 24 hours, 3) remove precipitate by centrifugation. The three categories of this fractionation scheme are illustrated below (Schnitzer, 1982).



Inevitably, nonhumic and inorganic substances will also be extracted by the procedure above. The fulvic acid fraction can contain some polysaccharide and low molecular weight compounds, highly lignified materials may be in the humic acid fraction, and inorganics can be common to all fra

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fractions (Hayes and Swift, 1978).

Organic matter can be extracted by other procedures than the classical one. Water, acids, bases, complexing agents, neutral salts, and organic solvents have also been used in soil organic matter extraction and characterization studies (Hayes and Swift, 1978). Schnitzer et al. (1958) compared a number of extractants for their ability to extract organic matter from the A and B horizons of a Podzol. The pH of the various solvents ranged from 1.4 to 13.1. Percent carbon extracted from the A horizon was extremely low for most of the extractants. Sodium hydroxide was the most quantitative for the A (24.3%) and had almost complete removal of the B horizon organic matter (96.3%). The majority of the extractants had efficiencies greater than 80% for the organic carbon extracted from the B horizon. These extractants included: sodium pyrophosphate at pH 7.0 and 9.8, NaF at pH 7.0 and 8.2, Na_3PO_4, $Na_2B_4O_7$, Na_2CO_3, HF, and Na_2-EDTA.

The identification of the organic substances in Spodosol profiles is obtained through both chemical and physical analysis. Elemental composition and functional group analysis provides valuable insight into the distribution of elements and to their importance in functional groups. Along with elemental and functional group analysis, the determination of molecular weight will allow one to piece together a possible arrangement of structural core units and functional groups in the humic substances. Because humic substances have an enormous complexity in their chemical composition, researchers have gone to degradative techniques in hopes of identifying their basic building blocks.

Elemental composition of humic substances extracted from a Podzol was reported by Schnitzer and Desjardins (1962) as follows:

horizon	C%	O%	H%	N%	S%
Ao	56.7	35.4	5.2	2.4	0.4
Bh	50.9	44.7	3.3	0.7	0.3

The lower carbon and higher oxygen contents in the Bh horizon is due to the higher oxidation stage of the humic substances. A comparison of fulvic acids extracted from B horizons of nine Podzols showed great similarity between them (Schnitzer, 1970). The ranges in carbon, hydrogen, nitrogen and oxygen were 44.2-49.0, 4.2-4.7, 0.7-1.1, and 45.7-50.3 percent respectively.

It is interesting to note that the second study included the Bh horizon reported in the first study. The carbon, oxygen, and hydrogen percentages did not fall within the ranges reported. There appear to be no major changes in the extraction or characterization procedures to account for this discrepancy.

A soil solution which was collected in a lysimeter placed between the Ae and Bhf horizons of a Podzol was also characterized for elemental composition (Schnitzer and Desjardins, 1969). Untreated and purified samples of the leachate gave different results. Composition of the purified sample fell within the ranges of carbon and oxygen reported in the study of nine Podzols mentioned above. The untreated sample had a much lower carbon percentage (41.5) but this sample was not discussed further. The authors claimed the leachate was mainly fulvic acid and that it was more characteristic of mobile soil organic compounds.

Soil organic compounds typically have carboxyl, hydroxyl (phenolic and alcoholic), carbonyl, and possibly quinone and methyoxy groups as their principal oxygen containing functional groups (Hayes and Swift, 1978). These are considered to be the most important groups due to the high percentage of oxygen within the humic substances. Schnitzer and Desjardins (1962) determined the following functional group content (milliequivalence/gram of organic matter) in the Ao and Bh organic matter.

horizon	carboxyl	phenolic-OH	alcoholic-OH	carbonyl
Ao	1.5	4.2	2.8	0.9
Bh	9.1	3.3	3.6	3.1

By the extraction and purification procedures used in this study the Ao organic substances would be characteristic of humic and fulvic acids whereas the Bh substances would be of a fulvic composition only. The high equivalent weight of carboxyl groups in the Bh horizon is consistent with the high amount of carboxyl groups found in most fulvic acids (Swift and Hayes, 1978). Using as a criteria the "ideal" humic and fulvic acids determined from a number of soils (Schnitzer, 1977) the functional groups in the humic substances in the A horizon fall within the range of an ideal humic acid and the Bh organic substances fall within the range of the ideal fulvic acid.

In order to integrate the elemental composition and the functional group analysis into a hypothetical structure of a soil organic compound in Spodosols one must also determine the molecular weight of the compound. Wright et al. (1958) determined the mean molecular weight of humic substances extracted from a Podzol B horizon. Using a solution of dialysed humic acid they reported the molecular weight to be 50,800. Schnitzer and Desjardin (1962) found the number-average molecular weight for Ao and Bh humic substances to be in the ranges of 1643-1726 and 663-690, respectively. A freeze-point depression method using sulfolane was used to determine the molecular weights. Khan and Schnitzer (1971) found spodic horizon fulvic acids tc be in the range of 175-3570 when using Sephadex gel filtration. Candler and VanCleve (1982) also used Sephadex gel filtration to determine a gross molecular weight approximation of the water extracted material from the B horizons of birch and aspen forest soils. The results reported suggested the molecular weights were 5000 and less.

Soil leachates have also been used for the determination of molecular weights of mobile soil organic compounds. Dawson et al. (1978, 1981) collected soil leachates in tension lysimeters placed in a number of horizons in two soil profiles. Ultragel and Sephadex gel filtration were used with a variety of standards. Interactions between gel and standards were noticed but a justification for their molecular weight determinations as being adequate was also given. Molecular weight of the major fractions from each horizon decreased with increasing soil depth. The molecular weights reported for the mobile soil organic compounds were 837-845 in a subalpine Podzol and 810-930 in a forest soil developed in glacial till. Schnitzer and Desjardin (1969) analyzed a soil leachate collected from the interface of the Ae and Bhf horizons of a Humic Podzol. After purification steps the molecular weight was reported as 492 by vapor pressure osmometry.

Schnitzer and Desjardin (1962, 1969) presented data on molecular formulae for Ao and Bh horizon humic material and for a purified soil leachate as:

Ao - $C_{75}H_{33}O_{17}N_3(COOH)_3(OH)_{12}(CO)_2$

Bh - $C_{21}H_{12}(COOH)_6(OH)_5(CO)_2$

SOIL LEACHATE - $C_{12}H_{22}O_2(COOH)_4OH(CO)_3$

The important distinctions to note are the high percentages of the molecular weight in the functional groups in the Bh and soil leachate material on the one hand and the low percentage in functional groups in the Ao horizon on the other hand. Also, the oxygen contained in the Ao humic substances is approximately evenly distributed between functional groups and the structural core. Both the Bh and the soil leachate have all or most of their oxygens in their functional groups.

Identification of low molecular weight compounds from humic substances extracted from Spodosol profiles has been achieved mainly by degradative techniques from which humic substances are broken down into monomeric units. Degradation of humic substances is accomplished by hydrolysis, oxidation or reductive methods (Schnitzer and Khan, 1972). The products of degradation are believed to consist of monomeric units which when identified and combined with data on bond linkages are expected to give a better picture of the original humic polymers (Felback, 1965). Monomeric units of a phenolic nature are also indications of source origin of which three have been identified: 1) flavanoids derived from plant materials, 2) phenolics from decomposition of lignin, and 3) metabolized products from microorganisms (Burges et al., 1964).

To appreciate the variety of methods involved in characterizing low molecular weight organic compounds that may be indigenous or degradative products, the methods used for extraction and/or characterization along with the compounds identified will be discussed in the following studies.

Water hydrolysis of the humic and fulvic acid fraction of a Podzol Bh horizon produced about one percent of the organic fraction as ether soluble phenolic compounds (Jakab et al., 1962). They also found their yields increased when using HCl, H_2SO_4 and $HClO_4$ and hydrolysing for 16 hours at 120°C. The ether extracts of the acid hydrolysed material represented 0.5 to 2.5 percent of the original organic matter. Phenolic compounds identified included: p-hydroxybenzoic, protocatechuic, and vanillic acids and vanillin. Similar products were also found when a lignin preparation was extracted in the same manner as the humic substances. This led the authors to conclude that the humic substances could contain lignin impurities. Jakab et al. (1963) later degraded the humic acids extracted from a Swiss Podzol Bh horizon with NaOH at 170 to 250°C in the presence and absence of $CuSO_4$. Over 30 phenolic compounds were detected which were suspected to be of lignin and microbial origin. The yields of phenolic compounds were found to be influenced by the temperature, for 6% of the total organic matter was attained at 250°C and only 2% at 170°C.

Coffin and DeLong (1960) characterized a Podzol B horizon collected from a profile located in a mature deciduous forest dominated by American beech. A soil sample was extracted 12 times using 8-quinolinol in benzene and pH 6.5 solution of water. Further separation of the 2 phases resulted in a combination of 6 fractions. The 6 fractions, 2 organic extracted and 4 aqueous extracted, accounted for approximately 75% of the soil organic matter. Carbohydrates and uronic acids were determined and one or both were found to be present in all fractions. The fraction containing the highest percentage (19.9%) of its organic matter as carbohydrates and uronic acids also gave evidence for galacturonic acid, glucose, galactose, arabinose, and xylose sugars after acid hydrolysis. The remaining fractions were degraded by potassium hydroxide fusion and extracted with ether and ethyl acetate. Using paper chromatography they were able to separate 19 phenolic compounds from the benzene fractions, 13 of which were acidic. The aqueous fractions yielded a total of 15 phenolic compounds, 5 of these being common to the benzene fractions. Identification of m- and p-hydroxybenzoic acids and 2,4 dihydroxy-benzoic acid were found in all fractions while 3,5 dihydroxy-benzoic acid was only determined in the aqueous fractions. These four phenolic acids accounted for 12 percent of the original soil organic matter. The authors noted that seven of the remaining compounds appeared to be of a similar concentration when compared to the standards of the compounds above. This would indicate that about 25 percent of the soil organic matter was of a phenolic composition. They also indicated a possible microbial origin of some of the phenolics for m-hydroxybenzoic and 3,5 dihydroxybenzoic acids are not believed to be lignin decomposition products.

Fulvic acids from Podzol Ao and Bh horizons were examined by Schnitzer and Wright (1960). Alkaline permanganate oxidation yielded several aliphatic carboxylic acids: oxalic, malonic, succinic, glutaric, adipic, pimalic, and suberic acids from the Ao and only oxalic acid from the Bh horizon. Three benzene carboxylic acids were present in the Ao: (1,2,3,4), (1,2,3,5), and (1,2,4,5) tetracarboxylic acids; and only one, pentacarboxylic, in the Bh. Nitric acid oxidation is less drastic and produced no evidence of oxalic acid, but did yield azelaic and the others mentioned above in the Ao. The Bh gave no oxalic and azelaic but did extract low yeilds of all the others. All four of the benzoic acids were found in both the Ao and Bh horizons. Picric acid was also found in the nitric acid oxidation products. This was believed to arise from nitric acid interaction with salicylic acid. The identification of aliphatic compounds in degradation methods are indications of saturated ring structures and/or longchain aliphatic structures. The benzene compounds are thought to be derived from polycyclic aromatic compounds. Schnitzer and Wright (1960) concluded the Ao horizon contained mostly aliphatic and/or alicyclic compounds with some aromatic substances, while the Bh organic matter consisted primarily of aromatic structures.

Jakab et al. (1962) using nitric acid oxidation was able to obtain 20 percent ether soluble products from a Swiss Podzol Bh humic acid. Contrary to the findings of Schnitzer and Wright (1960) only picric acid could be identified.

In a later study, Hansen and Schnitzer (1966) identified more benzene carboxylic acids from alkaline permanganate oxidation. These included: ortho, meta, and para-phthalic acids, (1,2,3), (1,2,4), (1,3,5) tricarboxylic acids, penta and hexa-carboxylic acids, as well as those mentioned in the study by Schnitzer and Wright (1960).

In a study of polyphenols in humus layers of Podzols, Coulson et al. (1960a) determined D-catechin, epicatechin, and kaempferol as well as several unidentified substances. They later extracted a Podzol B horizon with acetyl acetone and acid-hydrolyzed the resulting humic substances (Coulson et al., 1960b). Using one and two dimensional paper chromatography they found approximately 50 percent of the organic matter to be of polyphenolic origin.

Humic acids extracted from B horizons of two Podzols, one located in England and the other in the "pigmy" forest of California, were subjected to KOH fusion and/or NaOH-CuO oxidation (Steelink et al., 1960). Using paper chromatography they were able to find degradation products of catechol, protocatechuic acid, and resorcinol in the KOH mixture and catechol, vanillic acid, p-hydroxybenzaldehyde, 5-carboxybenzoic acid, vanillin, p-hydroxybenzoic acid, 5-carboxyvanillic acid, and 5-carboxyvanillin in the NaOH-CuO mixture. Several lignin products were found, which included catechol, protocatechuic acid, vanillic acid, vanillin, p-hydroxybenzoic acid. The authors tentatively identified resorcinol and phloroglucinol derivative and noted these are degradation products which relate in part to catechin, tannin, flavone and pinosylvan structures.

In a later study Greene and Steelink (1962) were able to obtain 20 percent ether soluble products using NaOH-CuO oxidation. Of this 20 percent they were only able to identify compounds that made up about 2 percent of the total organic matter. They identified vanillic, meta and para-hydroxybenzoic, and 3,5 dihydroxybenzoic acids and the aldehydes, vanillin, p-hydroxybenzaldehyde, and syringaldehyde. They concluded that the polyphenols of plant origin, other than lignin, were as significant as were those of lignin as possible sources of humus precursors. Microbial metabolites, many of which are derivatives of resorcinol and phloroglucinol, were also recognized as possible sources. Therefore, they believed humic acids were comprised of plant including lignin, and microbial phenolic compounds that copolymerize under oxidative conditions.

Burges et al. (1964) in a study to determine differences among humic acids from various soils, found that on the basis of their chromatographic pattern eight out of ten were easily distinguished. The humic acids were reduced by sodium amalgam for 3 hours at 100-110°C. The mixture was acidified and extracted with ether. By repeated ext

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extraction 30-35 percent of the original organic matter was recovered. Chromatography revealed a Podzol soil contained phenolic compounds of three origins. One was of possible flavanoid units which consisted of phloroglucinol, resorcinol, methylphloroglucinol, and 2,4 dihydroxybenzoic acid. A second was of lignin units that were assigned as p-hydroxybenzoic, vanillic, protocatechuic, and guaiacylpropionic acids. The third class of compounds were unassigned to any particular origin and were the compounds pyrogallol and 3,5 dihydroxybenzoic acid. To confirm the lignin assigned units the authors also analysed soil material from a lignin-free environment in Antarctica. They found a complete absence of all the lignin assigned units from this sample, thus confirming their hypothesis. They concluded that humic acids could be separated as to the origin of certain phenolic compounds based on either being of a deciduous hardwood or coniferous softwood source. The syringyl derivatives are formed under deciduous vegetation and vanillic acid predominates under coniferous softwoods where syringyl derivatives can be completely absent.

Tate and Anderson (1978) extracted humic acids from the Bh horizon of a Podzol and the A horizon of a Beech forest soil using 0.1 M sodium pyrophosphate. The humic acids were separated according to molecular size by gel filtration. The separated fractions were subjected to acid hydrolysis and the ether soluble compounds were analysed by gas chromatography. Phenolic acids detected included p-hydroxybenzoic, vanillic, and 3,4 or 3,5 dihydroxybenzoic acid. The higher molecular weight fractions produced the larger concentrations of the phenolic compounds. The low molecular weight fractions had insufficient material for analysis. They also extracted the A horizon with sodium hydroxide and analysed for phenolic acids using the same procedure as above. Contrary to the sodium pyrophosphate extracts the sodium hydrixide samples produced high concentrations of phenolic acids in the lower molecular fractions. Patterns of elution from gel chromatography separation showed distinctive differences between those humic acids extracted by the two solvents. The sodium hydroxide humic acids elution pattern gave two large peaks near the end of the elution capacity of the gel column. This represented lower molecular weight compounds that interact with the gel and take longer to elute. The pyrophosphate humic acids gave an elution pattern with a single large peak early in the elution. This suggested that sodium hydroxide may have caused the breakdown of the high molecular weight fraction. Although this may have been the case for the A horizon material, the Bh horizon was only extracted with pyrophosphate and the gel chromatography pattern produced resembled that of the sodium hydroxide extracted humic acids from the A horizon.

Separation of the 3,4 or 3,5 dihydroxybenzoic acid in the study by Tate and Anderson (1978) was not sufficient for absolute confirmation. Therefore, in a subsequent study (Anderson et al., 1978), the humic acids were analysed by gas chromatography-mass spectroscopy. Since both had the same retention time in the gas chromatography analysis, the use of mass spectroscopy would differentiate which was actually being detected. The mass spectrum data was a representation of the ions produced upon fractionation of the phenolic acid. They concluded that 3,4 dihydroxybenzoic acid was the actual phenolic acid extracted from the soils and confirmed this by a subsequent analysis using thin layer chromatography.

Low molecular weight alipathic acids were extracted from a wet Podzol pedon by separating into water and acid soluble fractions (Takeshima and Abe, 1978). The two fractions were adjusted to pH 2 and refluxed using ether for 72 hours at $< 50^{\circ}C$. Thirteen alipathic acids were used as standards for silica gel chromatography analysis and separated into six groups corresponding to their respective retention times. The alipathic acids determined in the soils were propionic, butylic, pyruvic, acetic, fumaric, glutaric, formic, tartaric, α-ketoglutaric, lactic, glycolic, oxalic, and citric acids. They found that water-soluble acids were less numerous with increasing depth but acid-soluble acids were more abundant with depth. The B2 horizon, which showed an accumulation of carbon, gave the highest content of acid-soluble as well as total alipathic acids in the soil pedon. They concluded the alipathic acids move downward through the soil profile with mineral constituents and accumulate in the B horizon in the form of salts.

Few studies have analysed the organic compounds in spodic horizons without some sort of degradation technique first. If the humic substances are immobilized in the spodic horizon then it would not be possible to extract with water and obtain results which characterize those immobilized organic compounds, for if they remained water soluble they would move out of the soil profile. Studies involved in surface horizon extraction using aqueous solvents have produced some evidence of free or water-soluble organic compounds which could possibly play a role in the podzolization process.

A soil developed in sand with a bracken fern cover was extracted with calcium oxide, filtered, acidified to pH 2, and analysed by one dimensional descending thin layer chromatography (Whitehead, 1964). Four acids were detected: p-hydroxybenzoic, vanillic, p-coumaric, and ferulic acids. Their concentrations ranged from $0.4\text{x}10^{-5}$ molarity for ferulic acid to $4.9\text{x}10^{-5}$ molarity for vanillic acid. These small concentrations are expected for the susceptability of these compounds to microbial degradation is great, and are easily leached or may readily react with other soil constituents. Besides reacting with several organic and inorganic constituents as well as being degraded by microorganisms these acids may influence the plant communities above ground which would ultimately affect the concentration of the plant produced phenolic compounds in the soil.

Evans (1980) found that with increased Podzol morphology the content of both carbohydrates and phenolic acids increased in the surface horizons. Four pedons representing various degrees of spodic horizon development were sampled. The surface horizon was collected from each site and extracted with water, and the carbohydrates were analysed directly while the phenolic acids were separated into an ether solution first. The carbohydrates were determined as a whole using the anthrone method and the phenolic acids were identified by gas chromatography. Carbohydrate concentration ranged from 90-1129 ug/g soil using a glucose standard. The phenolic acids were separated into major and minor constituents, which were represented by all four soils. No two soils contained the exact same type of minor or major constituents. Phenolic acids detected included: p-hydroxybenzoic, salicylic, vanillic, gallic, gentisic, sinapic, caffeic, protocatechuic, syringic, ferulic, and p-coumaric acids. The author suggested that both carbohydrates and phenolic acids increase as the proportion of coniferous to deciduous vegetation increase in the overstory.

In an attempt to reduce artifact formation, Khan and Schnitzer (1971) used several non-degradative methods in the analysis of a Podzol Bh horizon fulvic acid. First they separated the fulvic acid into molecular size fractions by gel filtration chromatography. The fractions were then methylated and further separated by thin layer chromatography. The zones located on the thin layer plates were scraped off and extracted with ethyl acetate. The ethyl acetate soluble compounds were analysed by gas chromatography, infrared, and mass spectroscopy. The three types of compounds found by this analytical procedure are: 1) alkanes and fatty acid methyl esters, 2) dialkyl phthalates, and 3) methoxy-benzene carboxylic acid methyl esters. The dialkyl phthalates accounted for approximately 80 percent of the compounds determined with the most prominent being bis (2-ethylhexyl) phthalate. The origins of each type of compound was also suggested. The first type, those of C_{14} to C_{26} alkanes and fatty acids, was believed to be of a microbial origin. The second type consisting of dialkyl phthalates was of uncertain origin but may have been from biosynthesis, plant compounds or fungal metabolites. The third type was suspected to be produced by either chemical and/or biological oxidation or lignin in the soil.

Although the findings discussed in this section are not in complete agreement, a general pattern does exist. It appears that most of the organic compounds identified, be it by degradation or water extraction, have aromatic structures and oxygen containing functional groups. The common groups include methoxy, carbonyl, carboxyl, and hydroxyl ligand groups which are potential sites for interactions with sesquioxides.

CHAPTER 2

CHARACTERIZATION AND CLASSIFICATION OF SOILS FROM MICHIGAN SPODOSOL SEQUENCES

G. F. VANCE and D. L. MOKMA

INTRODUCTION

Spodosols are the dominant soils within the majority of soil associations described in northern Michigan (Michigan Agricultural Experimental Station, 1981). Soils within these soil associations have morphological differences which are in part due to topographic and vegetative variations within the landscape. Spodosols have illuvial zones of amorphous complexes which are comprised of organic matter and sesquioxides (oxides of iron and aluminum). These zones are called spodic horizons and are usually identifiable in the field except in weakly developed soils for which additional tests are needed.

Chemical criteria have been developed to assist in the identification and classification of marginally developed soils. Soil Taxonomy (Soil Survey Staff, 1975) defines a procedure which utilizes sodium pyrophosphate extractable iron (Fep) and aluminum (Alp) and sometimes carbon (Cp), dithionite-citrate extractable iron (Fed) and aluminum (Ald), percent clay, and cation exchange capacity data to identify spodic horizons. Chemical criteria developed by the Canadian Soil Survey Committee (1978) use Fep, Alp, and percent clay as well as percent organic carbon to characterize Podzols, their equivalent of Spodosols. Recently, new chemical criteria using Cp, Alp, and Fep have been suggested (Mokma, 1983). These criteria have only been tested on a limited number of soils (Mokma and Buurman, 1982; Mokma, 1983). The three sets of chemical criteria are as follows:

Soil Taxonomy uses the following two ratio limits and accumulation index in defining the spodic horizon.

1) if $\mathrm{Fep} > 0.1\%$, then $(\mathrm{Fep} + \mathrm{Alp})/\mathrm{clay} \geqslant 0.2$ or

   if $\mathrm{Fep} < 0.1\%$, then $\mathrm{Cp} + \mathrm{Alp})/\mathrm{clay} \geqslant 0.2$,

2) $(Fep + Alp)/(Fed + Ald) \geqslant 0.5$, and

3) for all subhorizons that pass requirements 1 and 2 then

$$((CEC - \tfrac{1}{2}clay) \times \text{horizon thickness})$$

must be 65 or more for the profile.

The <u>Canadian System</u> requires that the Podzolic B horizon be at least 10 cm thick and meet one of the following,

A) to be classified as a Bh horizon the following characteristics must be met:

1. organic carbon $> 1\%$,
2. Fep $< 0.3\%$, and
3. organic carbon / Fep $\geqslant 20$.

or B) to be classified as a Bhf or Bf horizon the following characteristics must be met:

1. organic carbon $> 0.5\%$, (Bf contain 0.5-5% C and Bhf contain $> 5\%$ C),
2. Fep + Alp $\geqslant 0.6\%$ for textures finer than sand or $\geqslant 0.4\%$ for sand textures,
3. (Fep + Alp) / clay > 0.05, and
4. organic carbon / Fep < 20 or Fep $\geqslant 0.3\%$ or both.

The <u>new chemical criteria</u> requires the following characteristics to be met,

1) Fep + Alp + Cp must be greater in the illuvial horizons than the E horizon or A if no E is present,

2) Fep + Alp + Cp $\geqslant 0.50$,

3) have an atomic ratio of Cp / (Fep + Alp) between 5.8 - 25.0, and

4) for all subhorizons that pass requirements 1, 2 and 3, then

$$((Fep + Alp + Cp) \times \text{horizon thickness})$$

must be 5.0 or more for the profile.

Because of the apparent lack of a unified procedure for classifying Spodosols, this study evaluated the three sets of criteria and compared them to morphological characteristics.

MATERIALS AND METHODS

Three study areas containing ten pedons were selected for this study. The three areas were located in four counties within the northern half of Michigan's lower peninsula (Fig. 1). A hydrosequence and/or developmental sequence was sampled from within each study area: study area 1 - a hydrosequence, study area 2 - a developmental sequence, and study area 3 - a developmental sequence and hydrosequence. Well, moderately-well (study area 1), and somewhat poorly drained Spodosols were characterized for the hydrosequences. For the developmental sequences, three soils were sampled that represented different degrees of B horizon morphology: least developed having no spodic horizon, moderately developed having a Bs horizon and well developed having a Bh horizon.

At each site a soil pit was dug and the profile described according to the Soil Survey Manual (Soil Survey Staff, 1951). Soil samples were collected from the centers of each horizon within the profile. All physical and chemical analyses were done on air-dried, $<$ 2-mm soil materials. Particle-size analyses were carried out on mineral samples after the organic matter and cementing agents were removed. Organic matter was oxidized using 30% H_2O_2 and heating the sample in a sand bath. Cementing agents of iron and aluminum oxides were removed by sodium dithionite-citrate extraction following the method outlined by Soil Survey Staff (1972) with a slight modification to compensate for

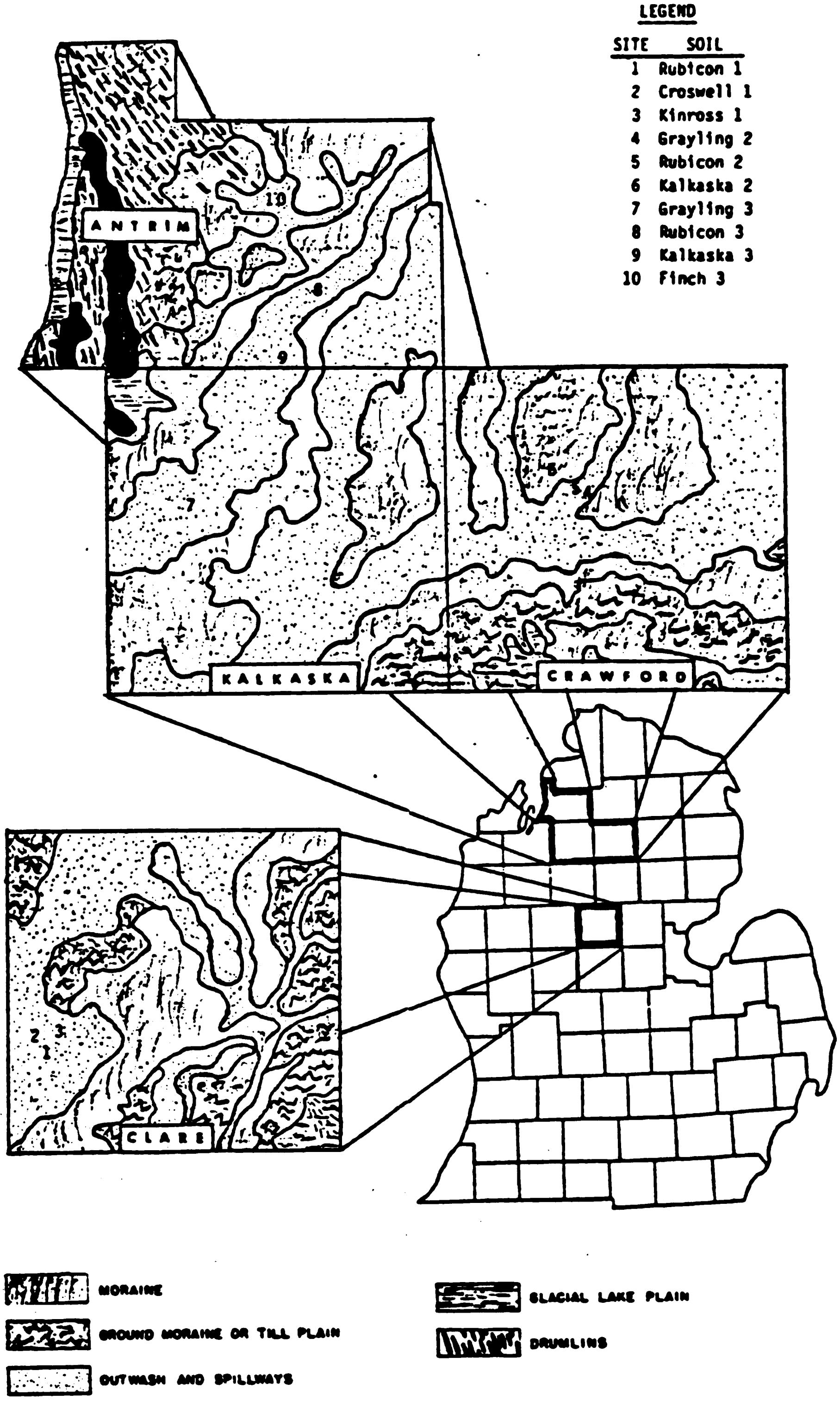

Figure 1. Location of the ten sites in the three study areas and their physiographical position.

the large volume of soil used for the particle-size analyses. Sieving was used for the fraction greater than 50 µm and the pipette method was used for the less than 50 µm fraction (Day, 1965).

Organic carbon was determined on samples that were ground to pass a 80 mesh sieve (0.10 mm). Quantification of organic carbon was by the dry combustion technique using a LECO Carbon Analyzer. Cation exchange capacity was determined by the method outlined by Warncke, Robertson, and Mokma (1980). Iron and aluminum were extracted by sodium dithionite and sodium pyrophosphate (Soil Survey Staff, 1972). Iron and aluminum were quantified by direct current plasma emission (Spectametrics, Inc.). Carbon was determined in sodium pyrophosphate, but, unlike the iron and aluminum extractions, no superfloc was added. Carbon was determined using a Dohrmann DC-50 Total Organic Carbon Analyser (Envirotech).

RESULT AND DISCUSSION

Soil Morphology

During the course of field mapping, a soil scientist must be able to identify soil properties, such as soil, color, texture, organic matter, clay content, structure, and others in order to delineate different soil areas (Olson, 1966). Therefore, it would be important to have a classification system in which these soil properties would assist the soil scientist in mapping. In coarse-textured soil materials the presence of a bleached (E) horizon and a dark brown or reddish B horizon is typically recognized as a Spodosol and would be mapped as such by the soil scientist.

The morphological characteristics of the ten pedons are given in Table 1. The locations of many of the pedons were as described for the typical pedon of that series taken from the county Soil Surveys. The

TABLE 1. Soil morphology and classification of the ten profiles.

HORIZON	DEPTH	COLOR		TEXTURAL		CONSISTENCE		ROOTS
	(cm)	matrix	mottles	CLASS	STRUCTURE		BOUNDARY	
Rubicon 1 (Entic Haplorthod, sandy, mixed, frigid)								
A	0-3	10YR2/1	---	ls	gr	vfri	ci	mf&m
E	3-9	10YR5/2	---	s	sg	loose	aw	cf
Bs1	9-35	7.5YR4/4	---	ls	sbk	vfri	cw	mf
Bs2	35-67	10YR4/4	---	s	sg	loose	gw	ff
BC	67-93	10YR5/6	---	s	sg	loose	cw	ff
C	93-150	10YR6/4	---	s	sg	loose	-	-
Croswell 1 (Entic Haplorthod, sandy, mixed, frigid)								
A	0-2	10YR3/1	---	ls	sg	loose	ai	mf&m
E	2-7	7.5YR6/2	---	s	sg	loose	aw	cf&m
Bs1	7-26	7.5YR4/4	---	s	sbk	vfri	cw	mf
Bs2	26-48	7.5YR5/6	---	s	sg	loose	cw	cf
BC	48-66	10YR6/6	7.5YR5/8	s	sg	loose	cw	ff
C1	66-100	10YR6/4	7.5YR5/6	s	sg	loose	cw	-
C2	100-125	10YR6/4	5YR5/8	s	sg	loose	-	-
Kinross 1 (Typic Haplaquod, sandy, mixed, frigid)								
A	0-4	10YR2/1	---	s	gr	vfri	as	mf&m
E	4-19	10YR6/2	---	s	sg	loose	aw	mf
Bs1*	19-32	7.5YR3/3	5YR4/4	s	sbk	vfri	cw	mf&m
Bs2*	32-51	7.5YR4/4	5YR4/6	s	sbk	vfri	cw	mf
C	51-73	10YR5/4	7.5YR4/4,5/6	s	sg	loose	-	-
* ortstein present, strongly cemented 2.5YR2/4 chunks in Bs1 and weakly cemented with 5YR3/2 interiors in Bs2.								
Grayling 2 (Typic Udipsamment, mixed, frigid)								
A/E	0-14	10YR4/2,6/2	---	s	sg	loose	aw	mf&m
Bw1	14-45	7.5YR4/6	---	s	sg	loose	gs	mf&m
Bw2	45-76	10YR5/6	---	s	sg	loose	cw	mf
BC	76-93	10YR6/4	---	s	sg	loose	ci	mf
C	93-150	10YR7/3	5YR4/8	s	sg	loose	-	-
Rubicon 2 (Entic haplorthod, sandy, mixed, frigid)								
A	0-5	10YR2/1	---	s	gr	vfri	aw	mf&m
E	5-15	10YR5/2	---	s	sg	loose	aw	cf
Bs1	15-31	5YR4/4	---	ls	sbk	vfri	ci	mf&m
Bs2	31-45	7.5YR4/4	---	ls	sg	loose	aw	mf
BC	45-82	10YR5/3	---	s	sg	loose	cw	ff
C	82-150	10YR5/4	7.5YR5/6	s	sg	loose	-	-
Kalkaska 2 (Typic Haplorthod, sandy, mixed, frigid)								
A	0-6	10YR3/1	---	ls	gr	vfri	cw	mf&c
E	6-15	10YR5/2	---	ls	sg	loose	aw	mf
Bh1	15-21	5YR3/2	---	sl	sbk	vfri	cw	mf&m
Bh2	21-32	5YR3/3	---	sl	sbk	vfri	aw	mf&m
Bsm*	32-60	7.5YR5/4	---	ls	m	vfi	aw	-
C*	60-150	10YR6/4	---	s	sg	loose	-	-
* strongly cemented matrix in Bsm, intermittent 10YR5/4 sand bands in C.								
Grayling 3 (Typic Udipsamment, mixed, frigid)								
A/E	0-8	10YR3/1,5/2	---	s	sg	loose	aw	mf&cm
Bw1	8-28	7.5YR4/6	---	s	sg	loose	gw	cf
Bw2	28-54	10YR5/6	---	s	sg	loose	cw	cf
C	54-150	10YR6/4	---	s	sg	loose	-	-
Rubicon 3 (Entic Haplorthod, sandy, mixed, frigid)								
A	0-6	10YR2/1	---	ls	gr	vfri	aw	mf
E*	6-21	7.5YR5/2	---	s	sg	loose	aw	cm
Bs*	21-51	7.5YR3/4	---	s	sbk	vfri	cw	cf
BC*	51-86	10YR5/6	---	s	sg	loose	gw	cf
C*	86-150	10YR6/6	---	s	sg	loose	-	ff
* chunks of weakly cemented albic material in E, strongly cemented ortstein chunks in Bs, 5YR4/6 sand bands in BC, discontinuous 5YR4/6 sand bands (3-10mm) spaced 5-10mm apart in C.								
Kalkaska 3 (Typic Haplorthod, sandy, mixed, frigid)								
A	0-9	10YR2/1	---	ls	gr	vfri	as	mf&m
E	9-23	10YR5/2	---	s	sg	loose	cw	cf
Bh	23-41	5YR3/2	---	s	sbk	vfri	ai	ff&m
Bs	41-83	7.5YR4/4	---	s	sg	loose	cw	ff&m
BC	83-88	10YR5/4	---	fs	sg	loose	cw	ff
C	88-150	10YR6/4	---	s	sg	loose	-	-
Finch 3 (Aeric Haplaquod, sandy, mixed, frigid)								
A	0-2	10YR2/1	---	s	sg	loose	aw	mf&m
E	2-23	10YR6/2	---	s	sg	loose	aw	mm
Bs*	23-35	5YR4/6	---	s	sg	loose	gw	cf
Bsm*	35-52	7.5YR5/6	2.5YR4/6,4/8	s	m	vfi	cw	ff
BC*	52-88	10YR5/4	2.5YR4/6,4/8	s	sg	loose	cw	-
C	88-101	10YR5/8	---	s	sg	loose	-	-
* strongly cemented ortstein chunks in Bs, strongly cemented matrix and few chunks of 5YR3/4 ortstein in Bsm, strongly cemented ortstein chunks in BC.								

soil classification in Table 1 is based on morphology, except for Kinross 1 which was originally classified as AuGres (Entic Haplaquod) but was changed due to the high carbon content in the spodic horizon. Eight of the ten pedons were classified as Spodosols, the remaining two appeared to have insufficient accumulations in the B horizons and were classified as Entisols. The Entisols are the Grayling 2 and Grayling 3 pedons.

All sites were forested and all but one of the pedons formed in glacial outwash with parent materials that contained greater that 95 percent sand. Kalkaska 2 was located on a glacial moraine. A lithological discontinuity was identified in this pedon between the B and C horizons. The C horizon has more than 95 percent sand and the B horizon has more than 20 percent silt. Although this pedon does not conform to the standards of uniformity in parent material throughout the sequence it was retained due to the Bh horizon which was used for the well developed member in the developmental sequence. No pedon could be found within the outwash materials that had a Bh horizon.

Chemical Characteristics

An important characteristic of Spodosols is the accumulation of organic matter, aluminum, and frequently iron in the spodic horizon (Soil Survey Staff, 1975). In all pedons except Grayling 2, the Fep and Alp show an accumulation in the B horizons (Fig. 2). With the Grayling 2 pedon the Fep percentage decreased with depth. The two pedons that were not identified as Spodosols, Grayling 2 and Grayling 3, were the only pedons not showing an accumulation of Cp in the B horizons. There is no evidence of eluviation and illuviation of humus and sesquioxides in these two pedons. All other pedons have translocation of C, Al and Fe. The B horizons of Kinross 1 have about twice as much or

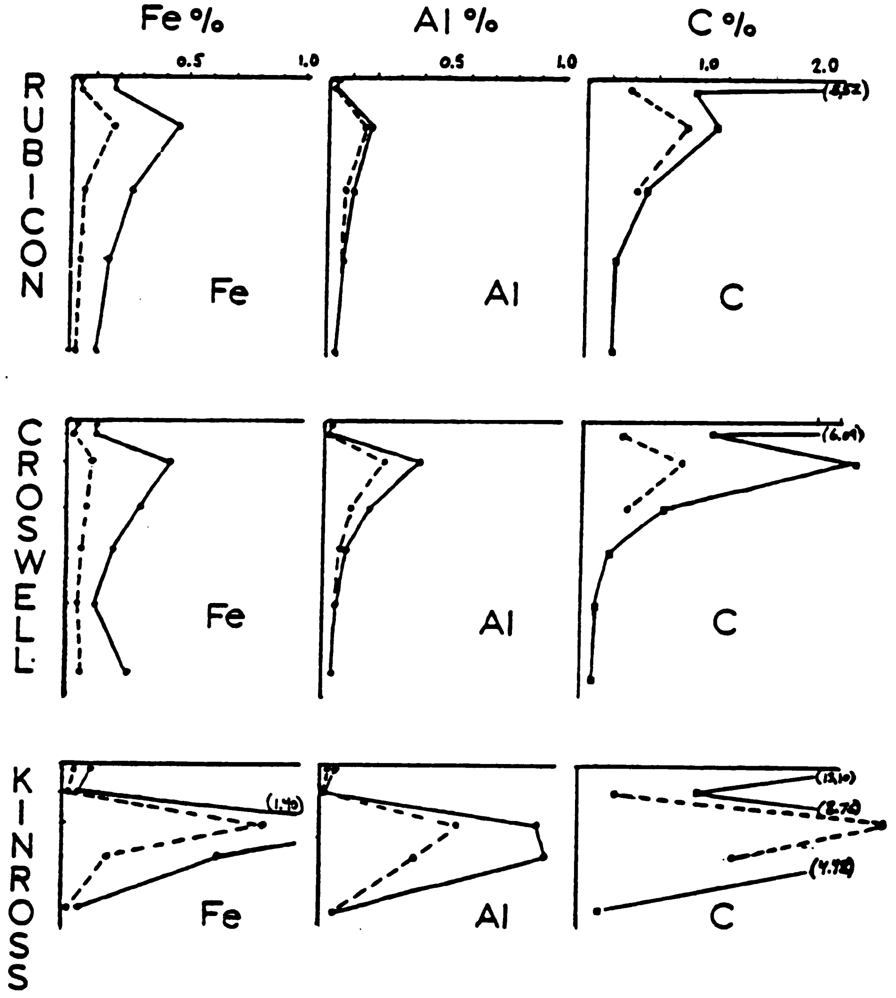

Figure 2. Profile distribution of sodium pyrophosphate extractable Fe, Al, and C, sodium dithionite extractable Fe and Al, and total carbon in sites of study area 1.

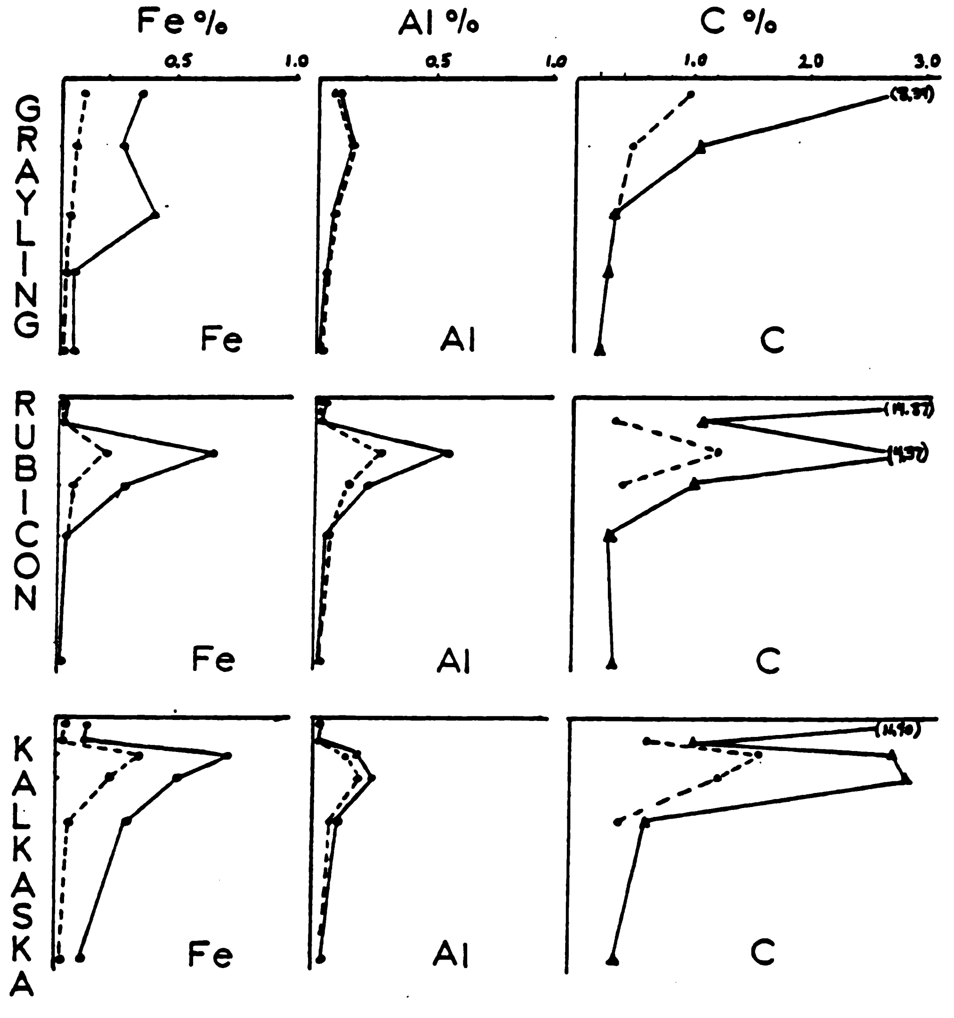

Figure 2. Profile distribution of sodium pyrophosphate extractable Fe, Al, and C, sodium dithionite extractable Fe and Al, and total carbon in sites of study area 2.

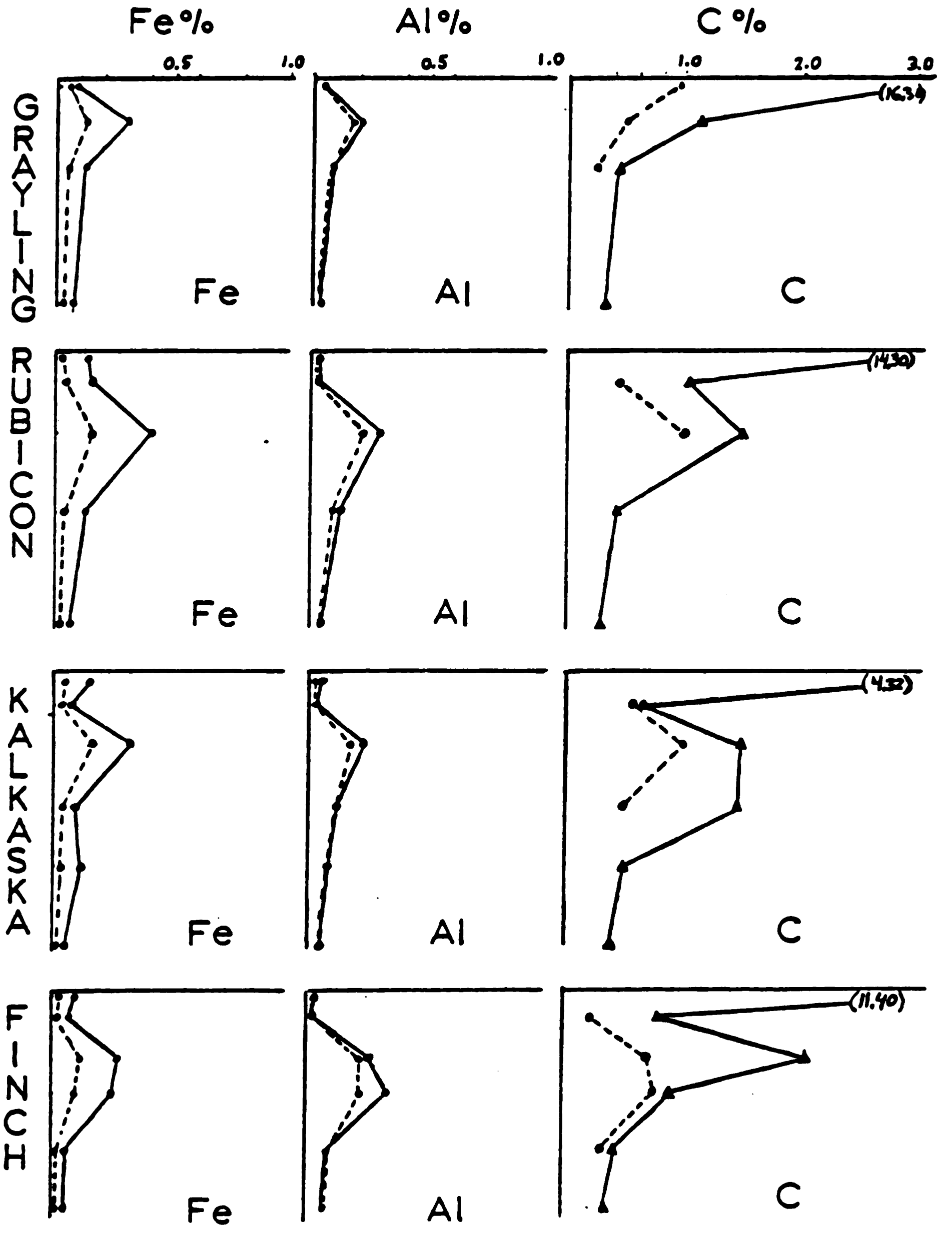

Figure 2. Profile distribution of sodium pyrophosphate extractable Fe, Al, and C, sodium dithionite extractable Fe and Al, and total carbon in sites of study area 3.

more of Fep, Alp, and Cp than do B horizons of the other pedons. This would indicate that the spodic horizon of this profile has a high concentration of pedogenic complexes.

Except for pedons Kinross 1 and Rubicon 2, there is little difference between the Ald and Alp, which suggests that the aluminum is primarily complexed with organic matter (Fig. 2). A large difference exists between the Fed and Fep in all pedons. This difference is commonly twice as much Fed as Fep. Similar results were also reported for Podzols in northern Alaska (Ugolini et al., 1982) and for a number of Podzols from temperate regions in the northern hemisphere (Mokma and Buurman, 1982). Thus, much of the iron present in the profiles is in the form of hydrous iron oxides.

Total organic carbon (Ct) was also contrasted to Cp (Fig. 2). A decrease in Ct occurs with depth in the two Grayling pedons. The remaining pedons show an accumulation of Ct as well as Cp in the B horizons. Kinross 1 contains an extremely high amount of Ct in the spodic horizon, especially in the Bs1 horizon. Chunks of ortstein in the Bs2 horizon of the Kinross 1 pedon showed Ct percentages closer to the Bs1 values that the Bs2 values. The ortstein sample also had higher Alp and Cp percentages but lower Fep, Fed, and Ald percentages than the Bs2 horizon.

In summary, the amounts of extractable iron, aluminum, and carbon increased as depth to the water table decreased and spodic horizon development increased. This would suggest there is a close relationship between the iron, aluminum, and carbon, as well as the physiographic and morphological characteristics in the landscape and pedon, respectively. The two pedons with no spodic horizon, Grayling 2 and Grayling 3, had low amounts of accumulation products and therefore, are classified as Entisols.

It appears that pedon Grayling 3 has some accumulations of organically bound iron and aluminum.

Soil Classification By The Three Chemical Criteria

Of the three sets of spodic horizon chemical criteria that were tested, two are used extensively for classifying the soils of North America that have spodic-like character. Many of these soils have morphological features that appear to show sufficient development to classify them as Spodosols. In several studies the chemical criteria outlined in Soil Taxonomy has been used and was found inadequate due to its stringent nature (DeKimpe and Martel, 1976; Joslin, 1978; Wang and Rees, 1980; Stanley and Ciolkosz, 1981; Mokma, 1983). In the study involving the new chemical criteria there was a soil that did not show spodic horizon morphology but was classified as a Spodosol according to Soil Taxonomy (Mokma, 1983).

Soil Taxonomy

Eight of the 10 pedons have been classified as Spodosols according to morphological features (Table 1). Of these eight pedons, only three, Kinross 1, Rubicon 3, and Kalkaska 3, meet the chemical criteria of Soil Taxonomy (Tables 2 and 3). With the Canadian System, five of the eight pedons showing spodic morphology met the chemical criteria. These include the three pedons that passed Soil Taxonomy criteria plus Croswell 1 and Rubicon 2. All eight pedons met the new chemical criteria. The two pedons that were classified as Entisols, Grayling 2 and Grayling 3, both failed all three sets of chemical criteria.

In the 10 pedons there are 20 B horizons that were tested and only five of these horizons met requirement 1 of Soil Taxonomy. Three of the five had Fep values less than 0.1%, thus Cp values were substituted for

Table 2. Physical and chemical data for the horizons that will be used in testing the spodic or podzolic chemical criteria.

HORIZON	TEXTURAL CLASS	HORIZON THICKNESS (cm)	CLAY (%)	CARBON (%)	CEC (meq/100g)	DITHIONITE CITRATE		PYROPHOSPHATE		
						Fe (%)	Al (%)	Fe (%)	Al (%)	C (%)
Rubicon 1										
E	s	6	1.9	0.89	2.9	0.18	0.02	0.04	0.02	0.39
Bs1	ls	26	5.7	1.09	7.1	0.46	0.18	0.18	0.16	0.83
Bs2	s	32	2.8	0.52	4.1	0.26	0.10	0.05	0.09	0.42
Croswell 1										
E	s	5	2.2	1.09	3.0	0.12	0.01	0.02	0.01	0.31
Bs1	s	19	4.0	2.28	9.3	0.44	0.40	0.10	0.25	0.81
Bs2	s	22	2.6	0.66	3.2	0.31	0.19	0.08	0.11	0.39
Kinross 1										
E	s	15	1.1	0.99	1.9	0.06	0.01	0.01	0.01	0.29
Bs1	s	13	5.8	8.76	27.8	1.40	0.92	0.86	0.58	2.71
Bs2	s	19	5.4	4.98	22.0	0.66	0.95	0.19	0.40	1.33
Grayling 2										
A/E	s	14	3.1	8.39	7.7	0.34	0.08	0.10	0.07	0.96
Bw1	s	31	3.5	1.02	4.2	0.26	0.14	0.06	0.14	0.43
Bw2	s	31	2.1	0.31	2.2	0.40	0.07	0.04	0.08	0.34
Rubicon 2										
E	s	10	1.2	1.09	4.0	0.01	0.01	0.01	0.01	0.35
Bs1	ls	16	6.3	4.37	17.8	0.66	0.56	0.20	0.28	1.21
Bs2	ls	14	5.2	1.01	10.3	0.28	0.22	0.06	0.14	0.40
Kalkaska 2										
E	ls	6	2.4	1.17	10.9	0.12	0.01	0.02	0.01	0.64
Bh1	sl	9	5.8	2.75	19.2	0.74	0.18	0.36	0.14	1.60
Bh2	sl	11	4.9	2.90	25.7	0.52	0.24	0.22	0.20	1.22
Bsm	ls	28	4.9	0.62	7.5	0.30	0.10	0.05	0.08	0.41
Grayling 3										
A/E	s	8	1.3	16.30	10.3	0.08	0.04	0.06	0.04	0.93
Bw1	s	20	3.1	1.16	6.7	0.30	0.20	0.12	0.18	0.47
Bw2	s	26	2.0	0.42	3.2	0.12	0.08	0.04	0.08	0.23
Rubicon 3										
E	s	15	1.5	1.04	3.0	0.16	0.02	0.04	0.02	0.44
Bs	s	30	2.3	1.46	8.1	0.41	0.29	0.16	0.22	1.00
Kalkaska 3										
E	s	12	1.6	0.64	6.6	0.08	0.02	0.04	0.02	0.58
Bh	s	18	3.1	1.43	11.7	0.33	0.22	0.17	0.18	0.99
Bs	s	42	1.2	1.36	2.7	0.09	0.11	0.04	0.11	0.49
Finch 3										
E	s	20	1.5	0.78	0.9	0.07	tr	0.01	0.02	0.22
Bs	s	12	3.7	2.05	6.2	0.28	0.26	0.12	0.22	0.71
Bsm	s	17	2.6	0.88	6.2	0.26	0.34	0.10	0.22	0.78

Table 3. Classification of the ten pedons according to the chemical criteria of Soil Taxonomy, Canadian System of Classification, and new criteria (Mokma, 1983).

	Soil Taxonomy				Canadian System				New Criteria			
Horizon	(1)	(2)	(3)	class†	(4)	(5)	(6)	class.	(7)	(8)	(9)	class.
Rubicon 1												
E	-	-	-		-	-	-		0.45	22.3	-	
Bs1	0.1	0.5	-	ns	0.3	0.06	6	np	1.17	7.5	30	s
Bs2	0.1	0.4	-	ns	0.1	0.05	10	np	0.56	8.3	18	s
Croswell 1												
E	-	-	-		-	-	-		0.34	35.4	-	
Bs1	0.1	0.4	-	ns	0.4	0.09	23	p	1.16	6.1	22	s
Bs2	0.1	0.4	-	ns	0.2	0.07	8	np	0.58	5.9	13	s
Kinross 1												
E	-	-	-		-	-	-		0.31	43.9	-	
Bs1	0.3	0.6	324	s	1.4	0.25	10	p	4.15	6.1	54	s
Bs2	0.1	0.4	-	ns	0.6	0.11	26	p	1.92	6.1	36	s
Grayling 2												
A/E	-	-	-		-	-	-		1.13	18.2	-	
Bw1	0.1	0.5	-	ns	0.2	0.06	17	np	0.63	5.7	-	ns
Bw2	0.2*	0.3	-	ns	0.1	0.06	8	np	0.46	7.7	-	ns
Rubicon 2												
E	-	-	-		-	-	-		0.37	53.0	-	
Bs1	0.1	0.4	-	ns	0.5	0.08	22	p	1.69	7.2	27	s
Bs2	tr	0.4	-	ns	0.2	0.04	17	np	0.60	5.3	-	ns
Kalkaska 2												
E	-	-	-		-	-	-		0.67	73.1	-	
Bh1	0.1	0.5	-	ns	0.5	0.09	8	np	2.10	11.4	19	s
Bh2	0.1	0.6	-	ns	0.4	0.09	13	np	1.64	8.9	18	s
Bsm	tr	0.3	-	ns	0.1	0.03	12	np	0.54	8.8	-	ns
Grayling 3												
A/E	-	-	-		-	-	-		1.03	30.3	-	
Bw1	0.1	0.6	-	ns	0.3	0.10	10	np	0.77	4.4	-	ns
Bw2	0.2*	0.6	57	ns	0.1	0.06	11	np	0.35	5.2	-	ns
Rubicon 3												
E	-	-	-		-	-	-		0.50	25.1	-	
Bs	0.2	0.5	209	s	0.4	0.17	9	p	1.38	7.6	41	s
Kalkaska 3												
E	-	-	-		-	-	-		0.64	33.1	-	
Bh	0.1	0.6	-	ns	0.4	0.11	8	p	1.34	8.5	24	s
Bs	0.5*	0.8	88	s	0.2	0.13	34	np	0.64	8.5	-	ns
Finch 3												
E	-	-	-		-	-	-		0.25	19.9	-	
Bs	0.1	0.6	-	ns	0.3	0.09	17	np	1.05	5.7	-	ns
Bsm	0.1	0.5	-	ns	0.3	0.12	9	np	1.10	6.5	19	s

* Cp was substituted for Fep

1) Fep+Alp/Clay

2) Fep+Alp/Fed+Ald

3) (CEC-Clay/2) x horizon thickness

4) Fep+Alp

5) Fep+Alp/Clay

† s=spodic, ns=non spodic, p=podzolic np=non podzolic

6) Ct/Fep

7) Fep+Alp+Cp

8) atomic ratio Cp/Fep+Alp

9) (Fep+Alp+Cp) x horizon thickness

Fep. The Bw2 horizons in both Grayling pedons had low Fep values, and when Cp percentages were used they both met requirement 1. The five horizons that met the first requirement of Soil Taxonomy are Kinross 1-Bs1, Grayling 2-Bw2, Grayling 3-Bw2, Rubicon 3-Bs, and Kalkaska 3-Bs. None of the Bh horizons of the two Kalkaska pedons met this requirement.

Soil Taxonomy's requirement 2 was met by 12 of the 20 B horizons with four of the five that met requirement 1 also meeting requirement 2. The one horizon that failed was that of the Bw2 horizon from Grayling 2 pedon. Of all the pedons, Croswell 1 and Rubicon 2 failed to classify as having a spodic horizon by requirement 2 alone. Therefore, most horizons which fail to meet the spodic horizon criteria of Soil Taxonomy failed to meet requirement 1.

Of the four B horizons that met requirements 1 and 2 the Bw2 horizon of Grayling 3 pedon did not have an adequate accumulation index. Thus, of the original 20 B horizons, 16 of which had morphological characteristics typical of spodic horizons, only three met all the chemical requirements of Soil Taxonomy.

Canadian System

Three of the B horizons qualify as Bh horizons in the Canadian System. They are Croswell 1-Bs1, Kinross 1-Bs2, and Rubicon 2-Bs1. Although Kinross 1-Bs1 had sufficient organic carbon and a ratio of Ct/Fep, it failed due to the high Fep value. Therefore, according to the Canadian System, the above three pedons qualify as Podzols with a Bh subhorizon.

For the remaining 17 B horizons not classified as Bh horizons, only the Bs1 horizon of Kinross 1 met the requirements of a Podzolic Bhf horizon. The Rubicon 3-Bs horizon and the Kalkaska 3-Bh horizon both qualify as podzolic Bf horizons.

The Bw2 horizons of both Grayling pedons failed the $>$ 0.5% minimum organic carbon content requirement of the Canadian System (Table 2). Subhorizons with finer than sand textures (Table 2) are required to have a higher value of Fep + Alp than that of sand. This requirement was the reason why the Kalkaska 2 Bh1 and Bh2 horizons failed to be classified as podzolic B horizons. The ratio of (Fep + Alp) / clay, used in Soil Taxonomy and also the Canadian System, but with a lower limit, was found to fail only two of the 20 B horizons. The two that failed were Bs2 of Rubicon 2 and Bsm of Kalkaska 3 pedons. Therefore, with the Canadian System, six of the 20 subhorizons qualified as podzolic B horizons which were found in five of the 10 pedons. Only in the Kinross 1 pedon did both Bs horizons qualify as being podzolic B horizons.

New Criteria

The new criteria successfully classified all eight pedons that showed Spodosol morphology as Spodosols and the two Entisol pedons as non-Spodosols. Both Grayling pedons failed due to higher Fep + Alp + Cp in the A/E horizon than the B horizons. Kalkaska 2-Bsm and Kalkaska 3-Bs horizons also fail this requirement. Only the Bw2 horizons of both Grayling pedons also fail to have at least 0.50 percent Fep + Alp + Cp.

Two of the 14 horizons that met the first two requirements failed to meet the minimum atomic ratio limit of 5.8. The two horizons are the Bs2 horizon of Rubicon 2 and the Bs horizon of Finch 3 pedons. Of the four Bw horizons in the two Grayling pedons only one, the Bw2 horizon of Grayling 2 pedon, meets the atomic ratio requirement.

For those horizons that qualify according to the accumulations of Fep + Alp + Cp and the atomic ratio all meet the illuviation index. This index assures that if the minimum amount of Fep + Alp + Cp is attained, the subhorizon must be 10 cm thick in order to qualify. No B horizon would have failed to meet the illuviation index.

To summarize the three chemical criteria placement of the soils, all three classified the Grayling soils, which do not have spodic horizons, as non-Spodosols or non-Podzolic soils and all three classified the same three pedons, Kinross 1, Rubicon 3, and Kalkaska 3, as Spodosols or Podzols. Two additional pedons were classified as Podzolic soils by the Canadian System whereas the new chemical criteria classified the remaining five pedons as Spodosols. The new chemical criteria correlated chemical analyses with soil morphological characteristics better than the two other criteria with the Canadian System showing a better correlation than Soil Taxonomy.

To the soil mapper, it is important that the morphological characteristics and chemical properties agree. This study suggests that the new chemical criteria have this advantage over the other criteria but only with additional testing will it be known if it is adequate in appraising spodic horizons.

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CHAPTER 3

EXTRACTION OF PHENOLIC COMPOUNDS FROM A SPODOSOL PROFILE : AN EVALUATION OF THREE EXTRACTANTS

G. F. VANCE, S. A. BOYD and D. L. MOKMA

ABSTRACT

Phenolic compounds were extracted from each horizon of a Spodosol profile by three extractants: 0.1 M sodium pyrophosphate at pH 7.0 and 10.2, and 0.5 N sodium hydroxide at pH 13.4. Of 28 standard compounds analyzed for 7 phenolic compounds were identified: three benzoic acids: protocatechuic, *p*-hydroxybenzoic, and vanillic acids; two aldehydes: vanillin and *p*-hydroxybenzaldehyde; and two cinnamic acids: *trans* *p*-coumaric and ferulic acids. The three most abundant compounds evaluated were protocatechuic acid, *p*-hydroxybenzoic acid, and vanillic acid. The amounts of each phenolic compound extracted increased with increasing extractant pH except for protocatechuic acid. Protocatechuic acid was extracted in the highest amounts by sodium pyrophosphate pH 10. The pyrophosphate (pH 10) extracts revealed that protocatechuic acid tended to accumulate in the B horizons suggesting that it may play a role in translocation of metal ions during podzolization. The two cinnamic acids, *trans* *p*-coumaric and ferulic were extracted primarily by NaOH. The identification of these cinnamic derivatives in a NaOH extraction of roots separated from the Bh horizon suggested that their presence may be due to degradation of plant residues by NaOH. Pyrophosphate (pH 7) extracted only low amounts of phenolic compounds. The specificity of pyrophosphate (pH 10) in removing organic complexes of a possible pedogenic nature suggests that it was the better extractant relative to soil genesis. Sodium pyrophosphate (pH 10) is recommended for use in future pedological studies of phenolic substances.

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INTRODUCTION

Low molecular weight aromatic compounds present in Spodosols have been studied for many years due to their possible role in solubilization and transport of metal ions during podzolization. Previous studies have demonstrated the presence of phenolic compounds, including phenolic acids and aldehydes in Spodosol surface horizons (Evans, 1980) and spodic horizons (Coffin and DeLong, 1960; Steelink et al., 1960). These compounds are thought to originate from roots of various plant species as well as leaf litter, and have been extracted and isolated from these sources (Whitehead et al., 1975, 1982, 1983).

Ideally, a pedogenic study of the organic compounds present in Spodosols should center on whole soil profile examination. However, previous studies of this nature involved the characterization of organic matter from only a single horizon; usually either a surface horizon or the spodic horizon. In our review of the literature we were unable to find a study in which all the horizons of a profile were studied for the purpose of characterizing the organic compounds present. Most of these centered around a number of soil samples taken from various profiles but not from entire profiles.

Extraction procedures must be a primary consideration following the selection of the soil profile. The nature of the material to be studied dictates which extraction procedure should be implimented. It has been shown that a high percentage of organic carbon can be recovered from spodic B horizons by the use of several different extractants including sodium pyrophosphate at pH 7.0 and 9.8, Na_3PO_4, $Na_2B_4O_7$, NaF at pH 7.0 and 8.2, Na_2CO_3, and NaOH (Schnitzer et al., 1958). The efficiency of these extractants in recovering organic carbon from surface horizons, however, is usually very low. Sodium hydroxide has been used widely as a general extractant in organic matter characterization studies but one major drawback to its use is the potential for oxidation and alteration of the indigenous soil organic compounds (Swift and Posner, 1972; Kaminsky and Muller, 1978). Sodium pyrophosphate is often a more effective extractant of pedogenic organics in spodic B horizons than is sodium hydroxide. This is due to the ability of pyrophosphate to form coordination complexes with metal ions such as iron and aluminum, which then allows the solubilization of organic compounds that were once complexed with these metal ions. Sodium pyrophosphate is considered to be a relatively mild extractant which minimizes the potential alteration of soil organics during extraction.

Extractant pH also needs to be considered in selecting an extraction procedure. Phenolic compounds have been extracted from a variety of surface horizons using aqueous extractants at various pHs (Whitehead et al., 1981). These extractants included water, 2N NaOH at pH 14, and graded amounts of $Ca(OH)_2$ added to water to adjust for pH levels in between. Low concentrations of phenolic compounds were detected in aqueous extractions at pH levels below their "threshold" limits. Once this limit was surpassed increased amounts of the phenolic compound were obtained with greater amounts recovered as pH was raised. In another study, the amount of organic carbon extracted from a surface and spodic horizon of a Podzol by sodium pyrophosphate at pH 7 was shown to be approximately 10 percent lower than that recovered at pH 10 (Schnitzer et al., 1958). Using nitrogen as an index of organic matter, Bremner and Lee (1949) demonstrated greater efficiency in organic matter extractability when sodium pyrophosphate solutions were raised from pH 4 to pH 9. Use of neutral sodium pyrophosphate in organic matter studies has been suggested to minimize potential chemical alterations of the soil organic matter (Bremner and Lee, 1949; Stevenson, 1982). However, pyrophosphate at pH 10 was found to extract organometallic complexes better than at pH 7 or pH 13 (Bascomb, 1968). Pyrophosphate at pH 7 also has the disadvantage of attacking crystalline minerals (Bascomb, 1968; McKeague, 1967).

After extraction of the organic components of interest, separation and identification is the next objective. High pressure liquid chromatography (HPLC) has been used successfully to identify phenolic compounds extracted from plants and soils (Hartley and Buchan, 1979). They suggest HPLC is approximately 10 times more sensitive than gas chromatography. Because of the greater sensitivity, estimations of small concentrations of phenolic compounds can be achieved with higher accuracy.

The objectives of this study were to: 1) identify and quantify the phenolic compounds extracted from each horizon of a Spodosol profile, 2) compare three extractants for their efficiency in extracting these compounds from the individual horizons, and 3) to evaluate the three extractants for their specificity towards removing possible pedogenic complexes. The extractants compared were aqueous sodium hydroxide and aqueous sodium pyrophosphate at pH 7.0 and pH 10.2. Recoveries of reference standards added to the soil horizons were also determined and used to calculate extraction efficiencies.

MATERIALS AND METHODS

Soil Material and Site Characteristics

Soil samples were collected on 31 November 1983 from six horizons of a Kalkaska sand (Typic Haplorthod, sandy, mixed, frigid) located in Kalkaska County, Michigan. The pedon was located on a sandy outwash plain of Wisconsin glacial material. Site vegetation consisted of silver maple (*Acer saccharinum*), sugar maple (*Acer saccharum*) and approximately ten percent hornbeam (*Ostrya virginiana*) in the overstory. Deciduous leaves covered the soil surface. Although no evidence of disturbance was detected, the forest did appear to be bimodal.

At the time of sampling, the soil materials were placed in plastic bags and then transported back to the laboratory and stored at $0^{o} \pm 2^{o}C$ until time of extraction.

Soil physical and chemical properties shown in Table 4 were determined on crushed air-dried samples which passed through a 2-mm sieve. After removal of organic matter and cementing agents particle size distribution was determined by sieving the greater than $50\mu m$ fraction and by pipetting the less than $50\mu m$ fraction (Day, 1965). Total organic carbon was determined using the dry combustion method (LECO Carbon Analyzer). Iron (Fep) and aluminum (Alp) were extracted by sodium pyrophosphate at pH 10 (Soil Survey Staff, 1972) and determined by direct current plasma emission (Spectametrics, Inc.).

Several soil properties of the Kalkaska profile are listed in Table 4. There is a maximal accumulation of illuvial clay in the upper spodic horizon but not enough to cause a change in textural class. Soil color and contents of organic carbon, Fep, and Alp indicate accumulation of organic matter with iron and aluminum in the spodic

Table 4. Some physical and chemical properties of the Kalkaska soil profile.

Horizon	Depth	Color (moist)	Particle size			Textural[a] class	pH[b]	Organic carbon	Fep	Alp
			sand	silt	clay					
	-cm-		-------	%	------			------ %	--------	
A	0- 9	10YR 2/1	85.0	11.7	3.3	ls	4.3	4.32	.05	.03
E	9- 23	10YR 5/2	90.1	8.3	1.6	s	4.2	0.64	.04	.02
Bh	23- 41	5YR 3/2	91.0	5.9	3.1	s	4.9	1.43	.17	.18
Bs	41- 83	7.5YR 4/4	97.6	1.2	1.2	s	5.0	1.36	.04	.11
BC	83- 88	10YR 5/3	98.8	0.8	0.4	s	5.1	0.49	.03	.08
C	88-125	10YR 6/4	99.1	0.5	0.4	s	5.1	0.38	.02	.04

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[a] Textural class according to USDA (Soil Survey Staff, 1951).

[b] 1:2.5 soil:water ratio

horizons. Organic carbon cantent is highest in the A horizon and second highest in the Bh horizon. Maximum Fep and Alp contents are present in the Bh horizon. The pH level is lowest in the eluvial zone (E) and gradually increases with depth.

Extraction Procedure for Phenolic Compounds

On the day previous to extraction, the soil samples were taken from storage and the less than 2-mm soil materials were separated by sieving. Any large root fragments found after sieving were discarded along with the greater than 2-mm soil materials. Approximately 70 grams of soil was weighed into 250 ml glass extracting vessels fitted with teflon lined caps. Small soil samples were also weighed to determine the moisture content so that all the soil weights could be calculated on an oven dry basis. To minimize the potential for artifact formation resulting from oxidative conditions during extraction the gas in the extracting vessel was exchanged with O_2 free N_2. Samples were stored under N_2 overnight at 2^oC. A Hungate apparatus was used for all gas exchange steps (Hungate, 1969). The following day, while constantly sparging with N_2, 100 ml of the extractant 0.1M sodium pyrophosphate at pH 7.0 (pyrophosphate (7)) or at pH 10.2 (pyrophosphate (10)) or 0.5 N sodium hydroxide at pH 13.4 (NaOH) were added to the extracting vessel. Prior to addition of the pyrophosphate (7) solution, the pH was lowered using phosphoric acid. All solutions were prepared using degassed distilled water.

After shaking for 18 hours, the samples were centrifuged for 25 minutes at 13,500 rcf using stainless steel centrifuge bottles. The supernatant was decanted and then acidified to pH 2.5 with 1N H_2SO_4 and centrifuged as above. The centrifuged material was then filtered by vacuum through a 0.45 micron silver membrane filter (Selas Flotronics, Penn.).

Separation of the phenolic compounds from the aqueous extracts was achieved by liquid-liquid extraction using diethyl ether. Three 60 ml volumes of ether were used. After the removal of the aqueous solution each ether phase was washed from the separatory funnel with water and combined in a round bottom flask. During ether separation an emulsion formed in those samples of the spodic horizons extracted with pyrophosphate. All emulsions were taken up with the ether phases. All samples were treated the same to eliminate any discrepancy between them. The combined ether phases (which contained water from the emulsion and the washings) were rotoevaporated at $<45^{\circ}C$ until free of ether. This solution was then transferred back to the separatory funnel and again extracted with ether. No evidence of emulsion was detected in any of the samples in this fourth separation. After removal of the aqueous phase the ether phase was washed from the separatory funnel and rotoevaporated ($<45^{\circ}C$) to approximately 3 to 10 ml volume, depending on horizon and extractant used. Samples were then placed in graduated tubes and analyzed immediately or stored at $0^{\circ} \pm 2^{\circ}C$ until analysis.

Chromatographic technique

HPLC was performed using a Waters System: high pressure pump (Model 60000A), variable wavelength UV detector (Model 480), data module integrator (Model 730) and a system controller (Model 720. A Rheodyne injector equipped with a 20 ul sample loop was used to inject samples. Reverse-phase chromatography was carried out using a Waters Bondapak C-18 steel column. An isocratic elution with a 1:15:984 mixture of acetic acid : N-butanol : water was used. Flow rate was 1.5 ml/min.

Chemical reference standards were purchased from Aldrich Chemical and used without further purification.

Identification and quantification of the phenolic compounds was achieved by matching retention times and peak areas to known standards. Table 5 lists the standards selected for comparison to the soil extracts and their respective retention times. This set of standards was chosen because previous workers had suggested their presence in soils. Some of the literature citations in which these compounds have been described are listed in Table 5. Three compounds: *o*-phthalic acid, γ-resorcylic, and protocatechuic aldehyde, were selected because of the close similarity in their chemical structure to some of the phenolic compounds found in soils. Standards were chromatogrammed at the initiation of this study. After determining which phenolic compounds were present in extracts from the Kalkaska soil, a mixture of these compounds was prepared and chromatogrammed at the start and end of each day's sampling run.

Recovery Experiment

Protocatechuic, *p*-hydroxybenzoic, and vanillic acids were added to each horizon to determine extraction effeciencies. A 10 ml aliquot, containing 100 µg of each acid, was added to approximately 70 grams of soil. Headspace gases were exchanged with N_2 prior to the addition of the test compounds. After addition of the standard solution, the soils were shaken by hand and then incubated stationary at 2°C for 24 hours. Extraction of the standards and the soil organics was as described in the extraction procedure section above.

Table 5. Retention times for Phenolic Standards and list of studies that identified the phenolic compounds in soils.

Compound	Retention time	Reference number
Benzoic Acids		
Gallic (3,4,5 triOH)[a]	3.15	9
Gentisic (2,5 diOH)	4.49	9
Phthalic (2 CO_2H)	4.92	—
α-Resorcylic (3,5 diOH)	5.08	2,4,6,24
Protocatechuic (3,4 diOH)	5.20	3,6,9,18,21
α-Resorcylic (2,6 diOH)	5.75	—
p-Hydroxy (4 OH)	8.23	3,4,9,11,21,25-28
m-Hydroxy (3 OH)	10.50	4
Vanillic (4 OH, 3 OCH_3)	11.11	3,9,11,18,21,24,25-28
Salicylic (2 OH)	13.75	9,19
Syringic (4 OH, 3,5 diOCH_3)	15.07	3,9,11,18,24,26
Benzaldehydes		
Protocatechuic aldehyde (3,4 diOH)	6.53	—
p-Hydroxy (4 OH)	9.41	11,26-29
Vanillin (4 OH, 3 OCH_3)	14.52	11,21,24,25-28
Syringaldehyde (4 OH, 3,5 diOCH_3)	21.23	23
Cinnamic Acids		
Caffeic (3,4 diOH)	14.12	9
cis *p*-Coumaric (4 OH)	18.10	9,11,18,24,25-28[b]
trans *p*-Coumaric (4 OH)	24.80	
Ferulic (4 OH, 3 OCH_3)	34.48	11,18,24,25-28
Sinapic (4 OH, 3,5 diOCH_3)	46.95	9
Phenols		
Guaiacol (2 OCH_3)	1.44	3
Phloroglucinol (1,3,5 triOH)	2.85	3,6,21
Pyrogallol (1,2,3 triOH)	2.95	3
Resorcinol (1,3 diOH)	4.45	3,6,21
Catechol (1,2 diOH)	5.39	20
Orcinol (1 CH_3, 3,5 diOH)	9.54	6
Catechins		
Dl-Catechin	11.68	5
Epicatechin	23.99	5

[a] Numbers and abbreviations in parenthesis represents location and type of functional group arrangement on the phenolic compounds.

[b] Several of these studies do not separate the *cis* and *trans* isomers.

RESULTS AND DISCUSSION

At the outset of this study it was presumed that pyrophosphate (7) would have the ability to extract organic compounds without substantial degradation of the indigenous humic substances (Stevenson, 1982) or alteration of the low molecular weight phenolic compounds. Pyrophosphate (10) was also evaluated because it is a commonly used extractant for analysis of iron and aluminum, which are believed to be complexed with soil organics (McKeague, 1967) and because it has recently been suggested for use in organic carbon determinations in Spodosol identification (Mokma, 1983). NaOH was selected because of its prevalent use in soil organic matter research.

The phenolic compounds extracted by all three extractants were: protocatechuic, p-hydroxybenzoic, vanillic, trans p-coumaric, and ferulic acids, and the aldehydes vanillin and p-hydroxybenzaldehyde. A chromatogram of the NaOH extract of the A horizon, and a solution containing authentic standards of the compounds listed above is shown in Fig. 3. Thus, 7 of the 28 standard phenolic compounds listed in Table 5 were identified in the NaOH and pyrophosphate extracts.

In general, pyrophosphate (7) extracted the lowest amounts of each compound and a lower total sum of phenolic compounds for each horizon when compared to pyrophosphate (10) and NaOH (Table 6). Pyrophosphate (10) usually extracted lower amounts of each compound and always had lower totals than NaOH. The ability to extract larger amounts of total phenolic compounds was typically in the order of pyrophosphate (7) $<$ pyrophosphate (10) $<$ NaOH. This follows a similar trend noted in the study of extractant pH (Whitehead et al., 1981) in which phenolic compounds were extracted in greater amounts at higher extraction pH.

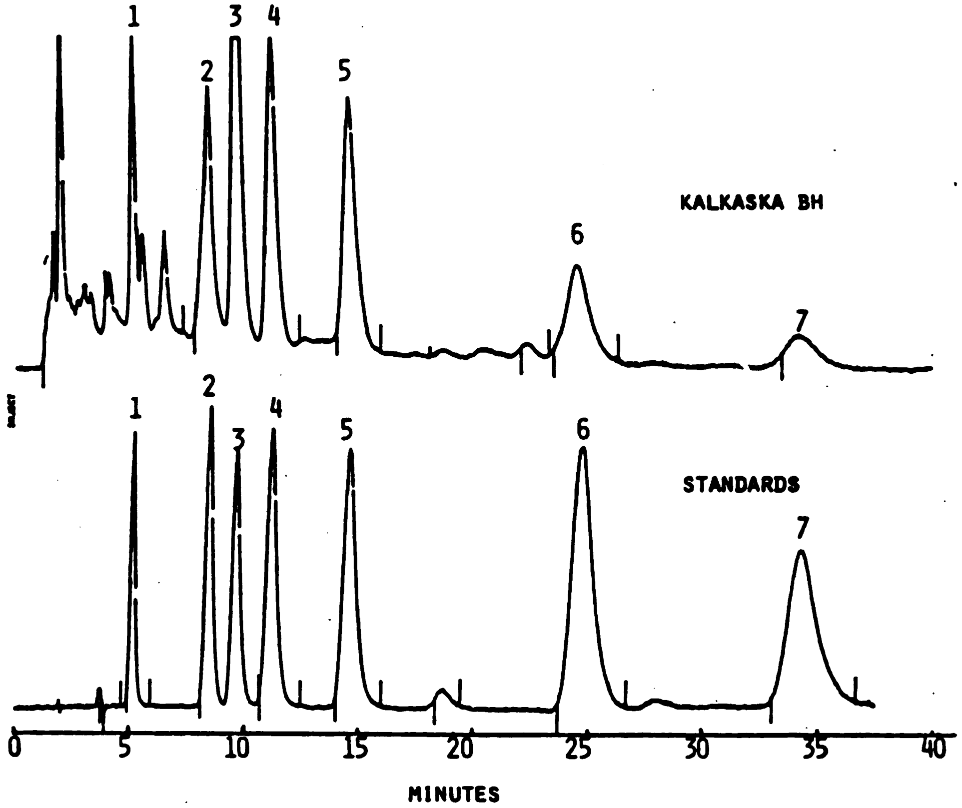


Fig. 3. Typical chromatogram of sample and standard. Peak numbers correspond to: 1) protocatechuic acid (3ppm), 2) p-hydroxybenzoic acid (6ppm), 3) p-hydroxybenzaldehyde (1ppm), 4) vanillic acid (6ppm), 5) Vanillin (3ppm), 6) trans p-coumaric acid (4ppm), 7) ferulic acid (5ppm). Numbers in parentheses are the concentrations used for the standards. Retention times of the compounds in the NaOH extract were identical to those in the standard solution ± 0.01 min.

Table 6. Concentrations of the phenolic compounds extracted from each horizon by the three extractants[a].

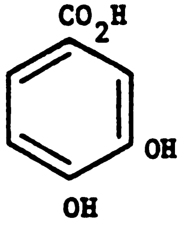
Horizon	Protocatechuic acid	p-Hydroxybenzoic acid	Vanillic acid	p-Hydroxybenzaldehyde	Vanillin	trans-p-Coumaric acid	Ferulic acid	Sum
Pyrophosphate (7)								
A	155(29)	157(29)	190(36)	14(3)	18(4)	0	0	534
E	16(36)	0	28(64)	0	0	0	0	44
Bh	63(23)	76(28)	124(46)	6(2)	tr[b]	0	0	269
Bs	86(41)	32(15)	82(39)	6(3)	6(3)	0	0	212
BC	6(21)	14(48)	9(31)	tr	tr	0	0	29
C	0	0	0	0	0	0	0	0
Pyrophosphate (10)								
A	233(16)	468(32)	612(42)	14(1)	52(4)	29(2)	42(3)	1450
E	36(28)	11(9)	64(50)	5(4)	12(9)	0	0	128
Bh	308(32)	209(22)	390(40)	27(3)	30(3)	tr	tr	964
Bs	324(47)	113(16)	191(28)	26(4)	37(5)	0	0	691
BC	71(48)	38(26)	24(16)	5(3)	10(7)	0	0	148
C	6(15)	15(38)	8(21)	2(5)	8(21)	0	0	39
NaOH								
A	2096(17)	2780(22)	3436(27)	1224(27)	1580(13)	828(7)	576(5)	12520
E	164(16)	199(19)	284(27)	108(10)	120(12)	44(4)	116(11)	1035
Bh	593(16)	734(19)	1331(35)	276(7)	408(11)	143(4)	318(8)	3803
Bs	608(26)	432(19)	696(30)	131(6)	170(7)	90(4)	175(8)	2302
BC	54(17)	110(35)	104(33)	15(5)	32(10)	0	0	315
C	0	41(43)	28(29)	8(8)	18(19)	0	0	95

[a] Data are expressed as ng phenolic compound/g soil. Numbers in parenthesis represent the amounts of a compound expressed as a percentage of the sum of phenolic compounds determined for that horizon.

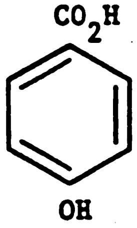
[b] Trace amounts. Peak area toolow to integrate accurately.

In that study pH was attained using various amounts of $Ca(OH)_2$ in water and a 2N NaOH solution. The only compound not determined by Whitehead et al. (1981) which was found in significant amounts in this study was protocatechuic acid. Protocatechuic acid, *p*-hydrobenzoic, vanillic, syringin, calicylic, *p*-coumaric, and ferulic acids have been detected previously in A horizons of forested soils (Shindo et al., 1978). Other studies, as referenced in Table 5, have also reported protocatechuic acid to be present in soils.

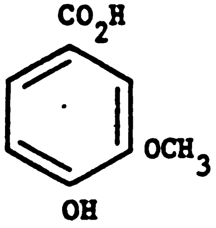
Percent recoveries of each of the three most abundant phenolic compounds: protocatechuic, *p*-hydroxybenzoic, and vanillic acids were determined for all horizons and extractants (Table 7). The structures of the phenolics used for the recovery experiment are shown below.



PROTOCATECHUIC
ACID



p-HYDROXYBENZOIC
ACID



VANILLIC
ACID

Recoveries for all three compounds from the A horizon were low. For *p*-hydroxybenzoic acid and vanillic acid, recoveries from the individual horizons of the profile appeared to be related to organic matter levels. Both pyrophosphate (7) and NaOH recovered low amounts of these acids from the A horizon, higher amounts in the E and then lower amounts in the Bh horizon. Low extraction efficiencies in the Bh horizon may have also been influenced by clay content. Thus, it appeared that the high organic matter contents of the A and Bh horizons accounted for the relatively low recoveries as compared to the E horizon. In contrast, pyrophosphate (10) recovered increasing amounts

Table 7. Percent recovery of standard components added to the soil [a].

Horizons	Protocatechuic acid			p-HydroxyBenzoic acid			Vanillic acid		
	$Na_4P_2O_7$(7)	$Na_4P_2O_7$(10)	NaOH	$Na_4P_2O_7$(7)	$Na_4P_2O_7$(10)	NaOH	$Na_4P_2O_7$(7)	$Na_4P_2O_7$(10)	NaOH
	%								
A	lr[b]	lr	lr	10	20	45	5	5	5
E	10	5	5	55	45	80	60	60	70
Bh	20	20	5	35	55	45	50	60	50
Bs	30	40	15	55	70	70	65	70	65
BC	15	50	15	75	70	70	75	75	70
C	lr	30	lr	80	85	80	40	80	80

[a] Percent recovered of amount added.

[b] lr = low recovery (< 5%).

of p-hydroxybenzoic acid and vanillic acid with increasing depth. The efficiency of extraction by pyrophosphate (10) was, therefore, not solely dependent on organic matter content.

Of the three phenolic acids tested, protocatechuic acid consistently gave the lowest recoveries demonstrating the effect that ortho-dihydroxy functional groups play in soil binding reactions. This may result from adsorption, chelation or oxidative coupling reactions with soil constituents. The pattern of recovery of protocatechuic acid in the individual soil horizons was different than that of p-hydroxybenzoic and vanillic acids in that it did not solely reflect the organic matter contents of the various horizons. For example, protocatechuic acid was recovered in higher amounts in the B horizons than in the E horizon. Sodium pyrophosphate (10) was the most effective extractant of protocatechuic acid. Sodium pyrophosphate (10) is known to extract organometallic complexes by complexing the metal ion and thereby releasing the organic ligand. Protocatechuic acid is capable of forming metal chelate complexes which would be extracted by pyrophosphate (10). Low recovery of protocatechuic acid in the A horizon by all extractants suggests that it has become rapidly and irreversibly bound perhaps as a result of oxidative coupling reactions with soil organic matter.

To summarize the recovery experiment, the results indicated that organic matter played an important role in the low recoveries of some phenolic acids, especially those in the free or non-complexed form. For these compounds, NaOH appeared to be the most effective extractant. For phenolic acids complexed to metallic cations such as Fe and Al, pyrophosphate (10) appeared to work best. The results also demonstrated that the horizons varied in their ability to bind phenolic substances and that the ortho-dihydroxy functional group of protocatechuic acid exerted a unique influence on extractability.

Concentrations of the extracted phenolic compounds identified in the soils of this study ranged from trace amounts up to a high of 3,436 ng of vanillic acid per gram of soil from the A horizon by NaOH extraction (Table 6). The pattern of total concentrations of phenolic compounds throughout the soil profile is similar to the pattern of organic carbon concentrations (Table 4). Spodosol profiles commonly have this pattern of organic carbon where high concentrations are found in the A and spodic horizons. Many profiles also have higher organic carbon concentrations in the E than in the BC horizons (Mokma and Buurman, 1982). This may be due to higher amounts of roots present in the E horizon. Both the pyrophosphate (7) and NaOH extractants produced patterns similar to that of the organic carbon whereas pyrophsophate (10) deviated slightly by extracting a higher sum total of phenolic compounds from the BC horizon than from the E horizon. Although the difference is approximately 15% higher total phenolic compounds in the BC than in the E horizon, with pyrophosphate (7) 50% more phenolic compounds are extracted from the E and with NaOH over 200% higher total phenolic compounds are extracted from the E compared to the amount extracted from the BC horizon. This suggests that pyrophosphate (10) extracts organo-metallic complexes, which are more prevalent in the BC than the E horizons, more selectively than pyrophosphate (7) or NaOH.

The quantity of each compound expressed as a percentage of the total sum of phenolic compounds determined for that horizon is also given in Table 6. This number can be used as an index of which individual phenolic compounds tended to accumulate in each horizon. The compounds with the highest percentages in each horizon varied somewhat with the different extractants. Vanillic acid was detected at higher percentages than were the other phenolic compounds in the upper horizons of the soil profile. The B and BC horizons generally gave higher percentages of protocatechuic acid. *p*-Hydroxybenzoic acid was found to be of the highest percentage in the C horizon. Especially noteworthy is the percentage of protocatechuic acid extracted by pyrophosphate (10) from the Bh, Bs, and BC horizons. With pyrophosphate (10) the percentage of protocatechuic acid increased threefold going from the A to Bs and BC horizons. When the amount of protocatechuic acid is weighted according to horizon thickness, then the amount of protocatechuic acid comprises 43% of the phenolic compounds present in the Bh, Bs, and BC horizons. It is important to understand that of the three most prevalent compounds extracted only protocatechuic acid is capable of chelating metal ions such as Fe and Al. Also, only with pyrophosphate (10) was the accumulation of protocatechuic acid in the B horizons observed. The accumulation of protocatechuic acid in the spodic horizons as well as accumulations of iron and aluminum (Table 1) would be consistent with the hypothesis that protocatechuic acid, iron, and aluminum migrate together in the form of organo-metallic complexes. Spodic horizons are zones of accumulated organic matter, iron and aluminum and several researchers have concluded that these accumulated products were translocated from the eluvial horizons as complexes. Immobilization in the spodic horizon is thought to result when the complex is saturated with additional cations or when changes in either ionic concentration or pH occur (DeConinck, 1980). Binding of the complex to soil particles or the polymerization of the organic constituents may also play important roles.

The NaOH extractants showed similar percentages of each phenolic compound in all horizons (Table 6). The consistent percentages of all seven phenolic compounds throughout the profile indicates NaOH may be extracting similar materials no matter which horizon is being extracted. trans *p*-Coumaric and ferulic acids were extracted mainly by NaOH, with pyrophosphate (10) extracting only small quantities from the A horizon and trace amounts from the Bh horizon. In a previous study these phenolic compounds were released from cell walls of grasses and legumes when treated with NaOH (Hartley and Jones, 1977). Whitehead et al., (1981) have shown that extractability of *p*-coumaric and ferulic acids from roots separated from surface soils was influenced greatly by pH; neither phenolic compounds was extracted from the roots of the surface horizons to any significant level until the extractant pH was greater than 10.5. This may explain why, in the present study, NaOH extracted large amounts of *p*-coumaric and ferulic acids whereas both these compounds were not extracted by pyrophosphate.

The difference between the amount of phenolic compounds which are extracted by NaOH versus pyrophosphate from the surface and spodic horizons could conceivably be attributed to the ability of NaOH to degrade plant materials and possibly the high molecular weight humic materials present in the soil. During filtration of the acidified NaOH extract it was noticed that no organic residues, such as small roots were left on the filters. However, both pyrophosphate extracts had these plant materials on the filters. Occurrence of these materials were noticed only in extractions of some of the horizons, especially the A and Bh horizons.

In a test of potential degradation of plant substances by NaOH, roots were washed from a sample of the Bh horizon and extracted with NaOH under N_2. A change in solution color occurred from a noncolored solution after the addition of NaOH to a yellowish brown color after shaking overnight. Phenolic compounds were extracted and chromatogrammed as previously described. All of the phenolic compounds detected in the NaOH soil extracts were also found in the NaOH root extracts. This suggests that the NaOH solution did degrade residues such as plant roots which would increase the concentration of the phenolic compounds determined. This could account for the higher amounts of phenolic compounds in the NaOH extracts. Degradation of plant materials, such as hemicellulose, lignin, carboyhdrates, and proteins can occur during NaOH extraction (Flaig et al., 1975). An exception to this finding is the higher amounts of protocatechuic acid found in the BC and C horizons of the pyrophosphate (10) extracts. This suggests that protocatechuic acid exists in a form more readily extracted by pyrophosphate (10), i.e., as a metal complex.

SUMMARY

All three extractants tested, pyrophosphate (7), pyrophosphate (10), and NaOH were able to extract phenolic compounds from a Spodosol profile. The amounts extracted were generally greater with higher extractant pH. The phenclic compounds identified were: *p*-hydroxbenzoic, protocatechuic, vanillic, *trans* *p*-coumaric, and ferulic acids and the aldehydes: vanillin and *p*-hydroxybenzaldehyde. Extraction of *trans* *p*-coumaric and ferulic acids was mainly by NaOH, which has been shown to be able to break down plant cell walls and release these phenolic compounds. Degradation of roots occurred during NaOH extraction.

Pyrophosphate (7) extracted low concentrations of the phenolic compounds and was unable to extract any of these compounds from the C horizon. The addition of phosphoric acid to neutralize the pryophosphate solution may have affected its ability to extract organic complexes. The possibility of dissolving crystalline minerals which would add ions to the extracting solution could conceivably increase complexation with the soluble organics and thus reduce the amounts of phenolic compounds extracted.

The evidence presented here indicates pyrophosphate (10) is a more useful extractant for estimating naturally occurring low molecular weight pedogenic phenolic compounds in Spodosol profiles. Increased efficiency in recovering added protocatechuic acid demonstrates the greater ability of pyrophosphate (10) to extract organic-metal complexes. Higher concentrations of protocatechuic acid were also extracted from the lower horizons in the Spodosol profile. The combination of the recovery data and the extraction of phenolic compounds from the soil suggests that pyrophosphate (10) is the better extractant for evaluating pedogenic complexes in Spodosol profiles.

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CHAPTER 4

PHENOLIC COMPOUNDS IN THE SOILS OF HYDROSEQUENCES AND DEVELOPMENTAL SEQUENCES OF SPODOSOLS

G.F. Vance, D.L. Mokma, and S.A. Boyd

INTRODUCTION

Pedologists generally agree that spodic horizon genesis involves the formation, translocation, and accumulation of organic-sesquioxide complexes. Several studies have shown that organic complexing agents, capable of solubilizing and transporting metal ions such as iron and aluminum, originate in the forest canopy (Coulson et al., 1960; King and Bloomfield, 1966; Malcolm and McCracken, 1968) and in the surface humus layer (Peterson, 1976). The characterization of canopy leachates and soil humic substances suggest phenolic compounds are involved in the podzolization process (Bloomfield, 1957; Coffin and DeLong, 1960; Tate and Anderson, 1978; Evans, 1980; Ugolini et al,. 1981). Forest canopy leachates can vary in both composition and amounts of water soluble phenolic compounds depending on the tree species (Malcolm and McCracken, 1968). Soils also contain a variety of phenolic compounds which can be retained unchanged at low concentrations or undergo coupling reactions to form humic substances.

Podzolization occurs at different rates under different tree species (Malcolm and McCracken, 1968; DeKimpe and Martel, 1976). Variable rates were also found under individual tree canopies within a given species (Crapmton, 1982). Evans (1980) has shown that low molecular weight phenolic compound contents increased in surface mineral horizons of Podzols as the proportion of coniferous to deciduous tree species in the forest overstory increased. The morphological expression of podzolization also increased.

The succession of both forest vegetation and soil development may occur congruently, for trees depend on the soil to supply moisture and nutrients; and soil development, especially podzolization, relies on the o

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organic compounds produced from canopy leachates and leaf litter decomposition. On coarse-textured soil in northern Michigan, forest succession typically proceeds from pioneer species (jack pine and aspen) to mid-successional species (red and white pine) to shade-tolerant species (sugar maple) (Spurr, 1973). These events may coincide with spodic horizon formation suggesting podzolization is influenced by the kinds of trees in the forest overstory. Typically, when pioneer species such as jack pine and aspens dominate forests, the soils found there have weak spodic horizon morphology. On the other hand, deciduous vegetation commonly indicates that stronger developed spodic horizons can be found at these sites.

The purpose of this study was to determine the low molecular weight phenolic compounds in soils of hydrosequences and developmental sequences of Spodosols. Hydrosequences and developmental sequences were selected in order to ascertain if low molecular weight phenolic compounds varied in composition or amount due to variations in vegetation and soil properties such as drainage.

MATERIALS AND METHODS

Site Descriptions

Ten soil pedons were sampled from forested sites within the northern half of Michigan's lower peninsula. These ten pedons comprise two hydrosequences and two developmental sequences which are located in three study areas (Fig. 4) - study area 1 is a hydrosequence, study area 2 is a developmental sequence, and study area 3 contains a developmental sequence and a hydrosequence. The hydrosequences consisted of well, moderately-well (study area 1), and somewhat-poorly drained Spodosols (Table 8). For the developmental sequences, three pedons were sampled

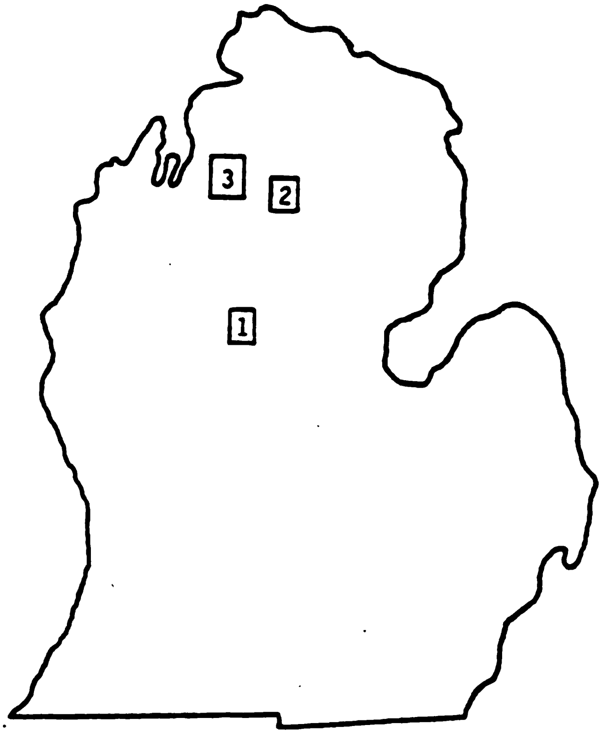


Fig.4. Location of the three study areas

Study area 1 - Clare County

Study area 2 - Crawford County

Study area 3 - Antrim and Kalkaska Counties

Table 8. Sequence characteristics in each study area and dominate overstory vegetation at each site. (tree species listed in order of dominance)

Site	Drainage class[a]	B horizons	Tree Species[b]
Study area 1 - hydrosequence			
Rubicon 1	WD	Bs	quaking aspen
Croswell 1	MWD	Bs	quaking aspen, sugar maple
Kinross 1	SWPD	Bs	sugar maple
Study area 2 - developmental sequence			
Grayling 2	WD	Bw	jack pine
Rubicon 2	WD	Bs	red pine, white pine
Kalkaska 2	WD	Bh,Bsm	sugar maple
Study area 3 - developmental sequence and hydrosequence			
Grayling 3	WD	Bw	jack pine, quaking aspen
Rubicon 3	WD	Bs	white pine, eastern hemlock
Kalkaska 3	WD	Bh,Bs	silver maple, sugar maple
Finch 3	SWPD	Bs,Bsm	bigtooth aspen

[a] WD - well drained, MWD - moderately well drained, SWPD - somewhat poorly drained.

[b] Scientific names :

bigtooth aspen	(*Populus grandidentata*)
quaking aspen	(*Populus tremuloides*)
eastern hemlock	(*Tsuga canadensis*)
silver maple	(*Acer saccharinum*)
sugar maple	(*Acer saccharum*)
jack pine	(*Pinus banksiana*)
red pine	(*Pinus resinosa*)
white pine	(*Pinus strobus*)

that represented different degrees of B horizon morphology; least developed having no spodic horizon, moderately developed having a Bs horizon, and a well developed having a Bh horizon. All the developmental sequence pedons are well drained.

Methods of Analysis

Particle size analysis was determined after organic matter and cementing agents were removed by H_2O_2 and dithionite-citrate extraction, respectively. The greater than 50-um fraction was sieved and the less than 50-um was pipetted following the procedure of Day (1965). The results are reported as textural class (Table 9) (Soil Survey Staff, 1951). The pH, total carbon, and sodium pyrophosphate extractable iron (Fep), aluminum (Alp), and carbon (Cp) were analysed on air-dried 2-mm soil materials. The pH was measured using a 1:2.5 soil to water ratio. Total carbon was determined by the dry combustion technique using a LECO Carbon Analyser. The Fep, Alp, and Cp were extracted by sodium pyrophosphate pH 10 using a 1:100 soil to solution ratio. The Fep and Alp were quantiatively determined by direct current plasma emmission (Spectametrics, Inc.) and Cp was determined using a Dohrmann DC-50 Total Carbon Analyser (Envirotech).

Soil samples that were used for the phenolic compound analysis had been stored at 0^{o}-2^{o}C from the day of field sampling. Low molecular weight phenolic compounds were extracted from the soils following the method described in the "Extraction procedure for phenolic compounds" section, chapter 3 using sodium pyrophosphate at pH 10. The "Chromatographic Technique" section in chapter 3 was followed for identifying and quantifying the extracted low molecular weight phenolic compounds.

RESULTS AND DISCUSSION

Soil-Vegetation Relationship

An apparent relationship between overstory vegetation and soil characteristics exists in three of the four sequences. In study area 1 the high degree of soil development and the influence of decreased depth to water table are reflected by increased sugar maples in the overstory. In the developmental sequences in study areas two and three, the vegetation - soil relations are similar to that described for coarse-textured soils in Michigan which is jack pine and aspen on least developed members, pines on moderately developed members, and maples on the well developed members. No relationship between overstory vegetation and soil characteristics was found in the hydrosequence in study area three. The Finch 3 site was dominated by aspen vegetation which is primarily a pioneer species, although large white pine stumps were identified at this site. This suggests that at one time the vegetation had progressed to a stage similar to the moderately developed members of the developemntal sequences. Being somewhat-poorly drained and having a firmly cemented B horizon may have hindered the growth of tree roots to that point and only shallow rooted tree species survived. However, there were sugar maples identified in the understory at the Finch 3 site.

Soil Materials.

Nine of the ten pedons formed in glacial outwash. The Kalkaska 2 pedon formed in glacial till. Most horizons had sand or loamy sand textures. Only the Bh horizons of Kalkaska 2 were sandy loam. The ten pedons have very strongly to extremely acid eluvial horizons (A and E) with gradual increases in pH with depth (Table 9). Total organic carbon is highest in the A horizon of all pedons with accumulations in

Table 9. Physical and chemical properties of the ten soil pedons.

SOIL PEDON	HORIZON	DEPTH (cm)	TEXTURAL CLASS	pH (H_2O)	TOTAL CARBON %	PYROPHOSPHATE Fe %	PYROPHOSPHATE Al %	PYROPHOSPHATE C %
RUBICON 1	A	0-3	ls	4.3	5.52	0.04	0.04	-
	E	3-9	s	4.6	0.89	0.04	0.02	0.39
	Bs1	9-35	ls	4.9	1.09	0.18	0.16	0.83
	Bs2	35-67	s	4.9	0.52	0.05	0.09	0.42
	BC	67-93	s	5.2	0.23	0.04	0.06	-
	C	93-150	s	5.0	0.21	0.02	0.03	-
CROSWELL 1	A	0-2	ls	3.9	6.09	0.04	0.03	-
	E	2-7	s	4.0	1.09	0.02	0.01	0.31
	Bs1	7-26	s	5.0	2.28	0.10	0.25	0.81
	Bs2	26-48	s	5.1	0.66	0.08	0.11	0.39
	BC	48-66	s	5.1	0.23	0.06	0.08	-
	C1	66-100	fs	5.1	0.10	0.05	0.06	-
	C2	100-125	s	5.1	0.09	0.06	0.04	-
KINROSS 1	A	0-4	s	3.8	13.10	0.04	0.04	-
	E	4-19	s	4.5	0.99	0.01	0.01	0.29
	Bs1	19-32	s	5.1	8.76	0.86	0.58	2.76
	Bs2	32-51	s	5.2	4.98	0.19	0.40	1.33
	Bs2ort*	-	s	5.1	7.39	0.11	0.47	1.64
	C	51-73	s	5.2	0.16	0.02	0.06	-
GRAYLING 2	A/E	0-14	s	4.3	8.39	0.10	0.07	0.96
	Bw1	14-45	s	4.8	1.02	0.06	0.14	0.43
	Bw2	45-76	s	4.9	0.31	0.04	0.08	0.34
	BC	76-93	s	4.9	0.27	0.02	0.04	-
	C	93-150	s	4.9	0.20	0.01	0.03	-
RUBICON 2	A	0-5	s	3.9	14.87	0.02	0.02	-
	E	5-15	s	4.3	1.09	0.01	0.01	0.35
	Bs1	15-31	ls	4.7	4.37	0.20	0.28	1.21
	Bs2	31-45	ls	4.5	1.01	0.06	0.14	0.40
	BC	45-82	s	4.5	0.29	0.03	0.06	-
	C	82-150	s	4.7	0.36	0.01	0.02	-
KALKASKA 2	A	0-6	ls	5.4	11.89	0.04	0.02	-
	E	6-12	ls	4.7	1.17	0.02	0.01	0.64
	Bh1	12-21	sl	4.8	2.75	0.36	0.14	1.60
	Bh2	21-32	sl	4.8	2.90	0.22	0.20	1.22
	Bsm	32-60	ls	5.0	0.62	0.05	0.08	0.41
	C	60-150	s	5.0	0.39	0.02	0.03	-
GRAYLING 3	A/E	0-8	s	4.0	16.31	0.06	0.04	0.93
	Bw1	8-28	s	5.2	1.16	0.12	0.18	0.47
	Bw2	28-54	s	5.3	0.42	0.04	0.08	0.23
	C	54-150	s	5.4	0.32	0.02	0.03	-
RUBICON 3	A	0-6	ls	4.4	14.31	0.02	0.02	-
	E	6-21	s	4.2	1.04	0.04	0.02	0.44
	Bs	21-51	s	4.6	1.46	0.16	0.22	1.00
	BC	51-86	s	4.8	0.41	0.04	0.10	-
	C	86-150	s	4.9	0.31	0.02	0.04	-
KALKASKA 3	A	0-9	ls	4.3	4.32	0.05	0.03	-
	E	9-23	s	4.2	0.64	0.04	0.02	0.58
	Bh	23-41	s	4.9	1.43	0.17	0.18	0.99
	Bs	41-83	s	5.1	1.36	0.04	0.11	0.49
	BC	83-88	fs	5.1	0.49	0.03	0.08	-
	C	88-150	s	5.1	0.38	0.02	0.04	-
FINCH 3	A	0-2	s	4.2	11.40	0.02	0.02	-
	E	2-23	s	4.2	0.78	0.01	0.02	0.22
	Bs	23-35	s	4.7	2.05	0.12	0.22	0.71
	Bsm	35-52	s	4.9	0.88	0.10	0.22	0.78
	BC	52-88	s	4.7	0.43	0.01	0.10	0.32
	C	88-101	s	4.7	0.38	0.01	0.08	-

*ortstein sample from Bs2 horizon

the spodic horizons. Biological activity in organic-rich surface horizons led to the formation of soluble organic acids which were partially responsible for the high acidity in eluvial horizons (Coleman and Thomas, 1967).

The amount of sodium pyrophosphate extractable iron (Fep) and aluminum (Alp) is greatest in the spodic horizons (Table 9). Both Grayling pedons lack spodic horizons but accumulations of Fep and Alp are present in the B horizons. The amount of Fep in Grayling 2 is highest in the A/E horizon. Organic carbon (Cp) extracted by sodium pyrophosphate was also high in the illuvial horizons that had high amounts of Fep and Alp. The Cp represents the portion of soil organic matter that is associated with organo-metallic complexes (Ugolini, 1982). Fep and Alp are also believed to be part of these organo-metallic complexes. The results of Fep, Alp and Cp indicate organo-metallic complexes have accumulated in the spodic horizons.

Phenolic Compounds

The low molecular weight phenolic compounds extracted include protocatechuic acid (3,4-dihydroxybenzoic acid), *p*-hydroxybenzoic acid (4-hydroxybenzoic acid), vanillic acid (4-hydroxy-3-methoxybenzoic acid), *p*-hydroxybenzaldehyde (4-hydroxybenzaldehyde), vanillin (4-hydroxy-3-methoxybenzaldehyde), *trans* *p*-coumaric acid (4-hydroxycinnamic acid), and ferulic acid (4-hydroxy-3-methoxycinnamic acid) (Table 10). Identification was achieved by matching retention times of the extracted compounds with those of standard compounds. The retention times of the extracted compounds were identical to those of the standard compounds by ± 0.01 minutes.

Concentration of the individual phenolic compounds ranged from

Table 10. Amounts of phenolic compounds extracted from each horizon of the soils within the hydrosequences and developmental sequences.[a]

HORIZON	Protocatechuic acid	p-Hydroxybenzoic acid	Vanillic acid	p-Hydroxybenzaldehyde	Vanillin	trans-p-Coumaric acid	Ferulic acid	Total
RUBICON 1								
A	5	1020	350	30	100	110	50	1660
E	5	270	110	10	20	5	0	410
Bs1	90	190	90	10	30	0	0	410
Bs2	50	100	20	10	10	0	0	190
BC	30	20	20	5	5	0	0	70
C	20	10	20	5	5	0	0	50
CROSWELL 1								
A	0	330	130	0	0	0	0	460
E	10	200	150	5	10	0	0	370
Bs1	210	280	160	20	20	0	0	690
Bs2	80	100	40	10	10	0	0	240
BC	40	30	30	5	10	0	0	110
C1	30	10	20	5	10	0	0	70
C2	5	10	20	5	5	0	0	30
KINROSS 2								
A	140	300	180	10	20	20	0	670
E	30	80	20	5	10	0	0	140
Bs1	420	370	310	10	40	0	0	1150
Bs2	290	240	150	10	30	0	0	720
Bs2ort*	430	180	240	10	20	0	0	880
C	20	10	10	5	0	0	0	40
GRAYLING 2								
A/E	180	300	630	20	70	30	20	1250
Bw1	70	60	80	20	20	10	0	260
Bw2	60	20	30	10	10	0	0	130
BC	10	10	5	5	5	0	0	20
C	10	10	5	5	5	0	0	20
RUBICON 2								
A	210	120	260	0	0	0	0	590
E	50	30	90	5	0	0	0	170
Bs1	440	170	380	20	60	10	30	1110
Bs2	200	50	140	10	50	0	0	450
BC	30	10	30	5	10	0	0	80
C	20	10	10	5	5	0	0	40
KALKASKA 2								
A	10	950	370	5	70	130	50	1580
E	0	150	130	0	20	0	0	300
Bh1	260	290	310	0	50	0	0	910
Bh2	320	270	280	10	60	0	0	940
Bsm	70	20	30	5	30	0	0	150
C	10	10	10	5	10	0	0	40
GRAYLING 3								
A/E	60	280	350	30	30	30	0	780
Bw1	100	60	60	30	20	0	0	270
Bw2	30	10	10	5	10	0	0	60
C	10	5	0	5	0	0	0	10
RUBICON 3								
A	50	430	410	0	40	90	0	1020
E	80	90	170	10	30	20	0	400
Bs	330	80	160	20	50	10	0	650
BC	70	20	40	5	10	0	0	140
C	20	5	10	0	0	0	0	30
KALKASKA 3								
A	230	470	610	10	50	30	40	1440
E	40	10	60	10	10	0	0	130
Bh	310	210	390	30	30	5	5	970
Bs	320	110	190	30	40	0	0	690
BC	70	40	20	10	10	0	0	140
C	10	20	10	5	10	0	0	50
FINCH 3								
A	390	800	470	20	30	50	0	1760
E	90	230	80	20	20	0	0	440
Bs	470	230	180	30	60	0	0	970
Bsm	160	100	60	10	20	0	0	350
BC	120	100	60	10	10	0	0	300
C	90	60	60	10	10	0	0	230

[a] Data expressed in ng phenolic compounds/gram oven dry soil weight.

0 to 1020 ng/g soil with protocatechuic, p-hydroxybenzoic, and vanillic acids accounting for the largest amount of phenolic compounds in each horizon. Protocatechuic acid was typically found in the highest concentration in the B horizon. The major phenolic compounds identified in a Kauri Podzol Bh horizon were also protocatechuic, p-hydroxybenzoic, and vanillic acids with protocatechuic acid present in the highest concentration (Tate and Anderson, 1978).

In this study, only Grayling 2 had protocatechuic acid higher in the A horizon than in the B horizons which may be related to the fact that this is a weakly developed Spodosol (Table 9). Conversely, both p-hydroxybenzoic and vanillic acids were generally found in higher concentrations in A horizons. This suggests that protocatechuic acid has a greater ability to migrate and accumulate in subhorizons than do p-hydroxybenzoic and vanillic acids.

The benzaldehydes, vanillin and p-hydroxybenzaldehyde, were extracted in low amounts from all pedons, with the highest concentrations generally found in the surface horizons (Table 10). Of the two benzaldehydes, vanillin was always the most abundant. For the benzoic acid derivatives, p-hydroxybenzoic acid was generally found to be more abundant than vanillic acid. These four compounds, p-hydroxybenzaldehyde, vanillin, p-hydroxybenzoic acid, and vanillic acid, have been identified in soils, roots, and leaf litter in several studies (Hartley and Buchan, 1979; Whitehead et al., 1981; 1982; 1983). Benzaldehydes were extracted from wood of coniferous trees (Ribereau-Gayon, 1972). Vanillin made up 94% of the benzaldehydes from a conifer lignin sample (Creighton, 1974 in Crawford, 1981).

Fourteen of the 56 horizons contained trans p-coumaric acid while only six of the horizons contained ferulic acid (Table 10). Katase (1981) found low concentrations of these cinnamic acids in free form in a surface horizon of a forested soil in Japan. Low concentrations of these acids were also found in soils extracted by 1% calcium oxide (Whitehead, 1964) and 0.1 M sodium pyrophosphate (Guenzi and McCalla, 1966).

Total concentrations of the phenolic compounds varied from 10 ng/g soil in the C horizon of Grayling 3 to 1760 ng/g soil in the A horizon of Finch 3 (Table 10). B horizon accumulations occurred in seven of the ten pedons as indicated by lower concentrations in the overlying E horizons. The two Grayling pedons and Rubicon 1 had decreasing amounts with depth. Generally, the surface horizons have the highest total concentrations of phenolic compounds. Kinross 1 and Rubicon 2 had the highest spodic horizon total concentrations. Both of these pedons also had low concentrations in their A horizons.

The amounts of phenolic compounds determined in this study are lower than those, 34 to 632 ppm (34-632 x 10^3 ng/g soil), reported by Shindo et al. (1978) for NaOH extraction of O, A, and B horizons from some forested soils. The difference in amounts extracted can be attributed to the use of different extractants. The amount of phenolic compounds increased with increasing extractant pH (Whitehead et al., 1981). Highest concentrations were found in sodium hydroxide extracts (see chapter 3 of this thesis).

The relationship between concentrations of the major phenolic compounds and pedon horizons are shown in Fig. 5. Generally, these compounds are present in higher quantities in the A and spodic horizons as compared to the E horizons. These differences are accentuated as

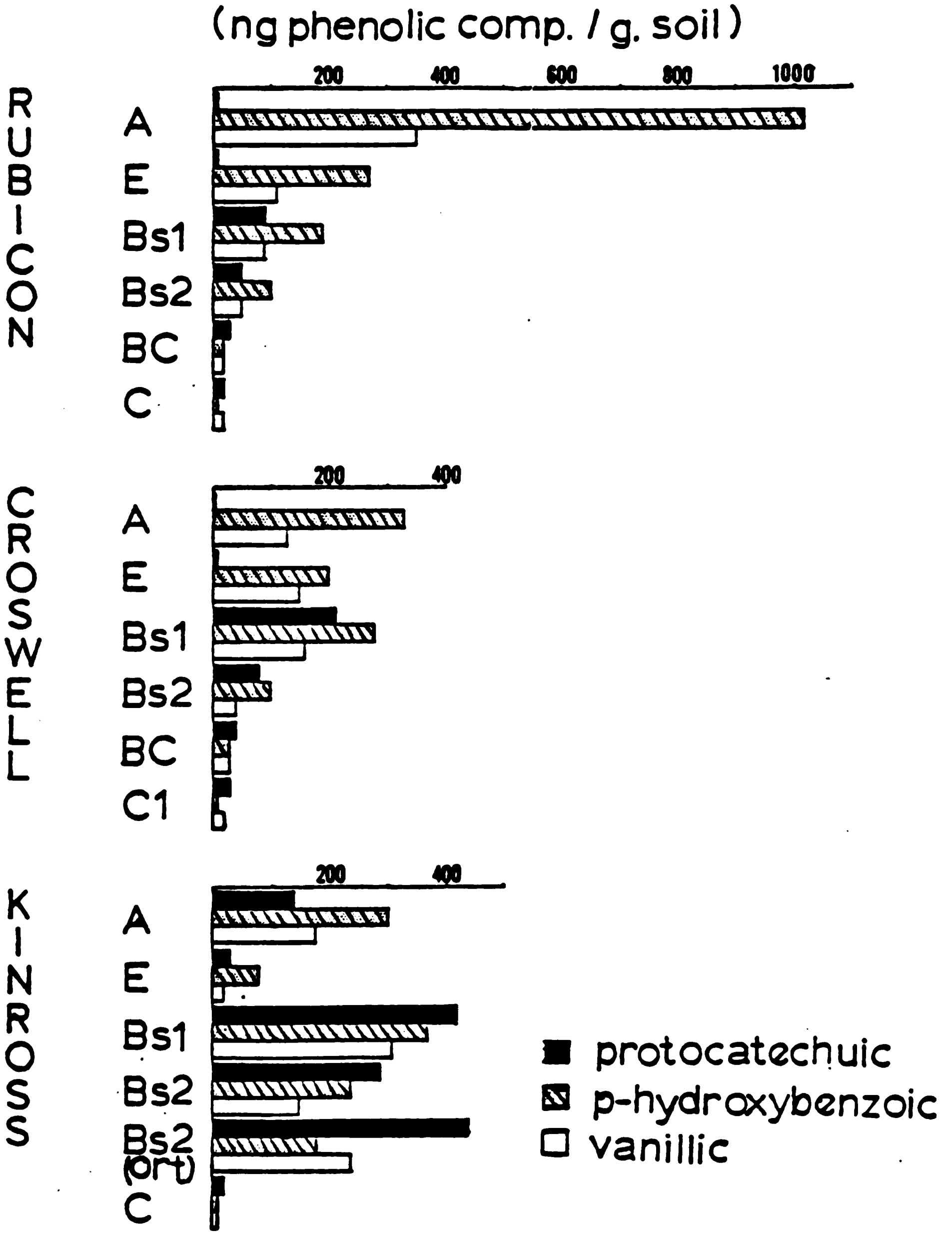


Figure 5. Profile distribution of protocatechuic, p-hydroxybenzoic, and vanillic acids for pedons of study area 1.

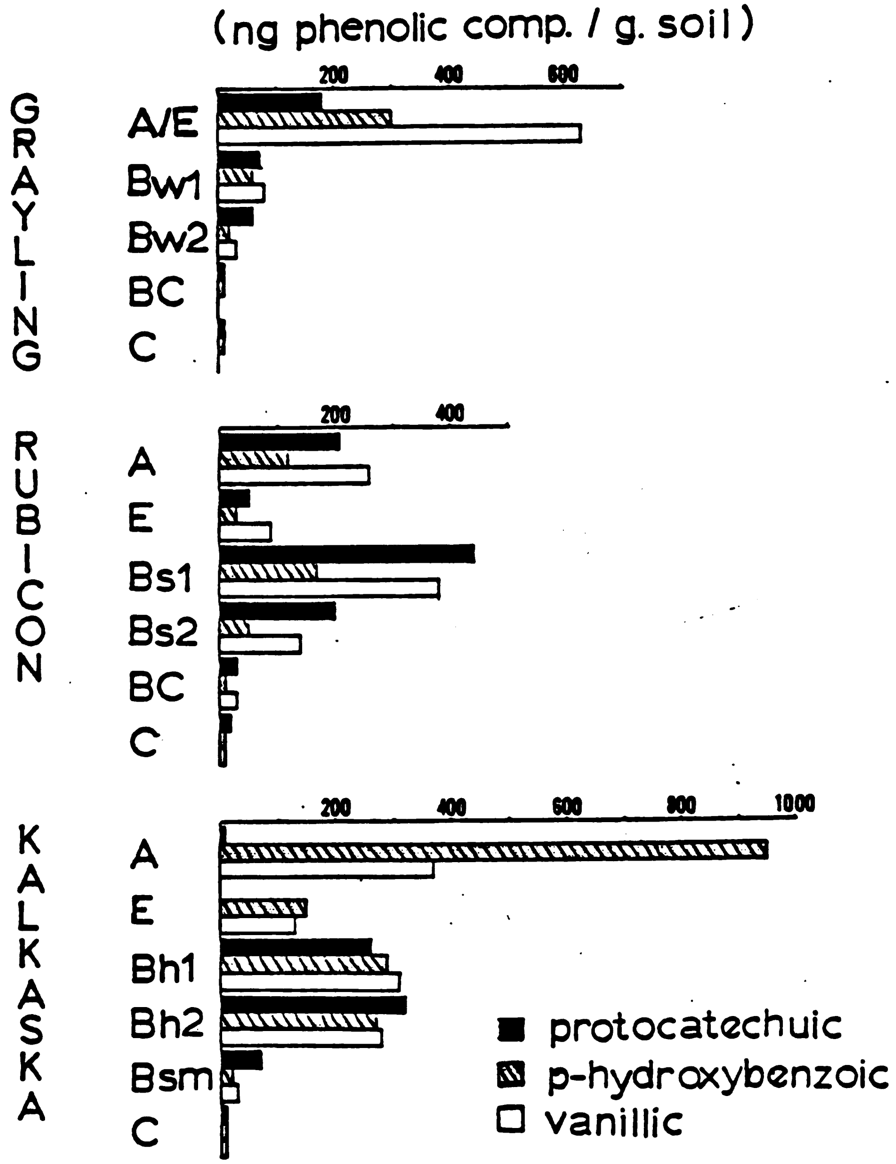


Figure 5. Profile distribution of protocatechuic, p-hydroxybenzoic, and vanillic acids for pedons of study area 2.

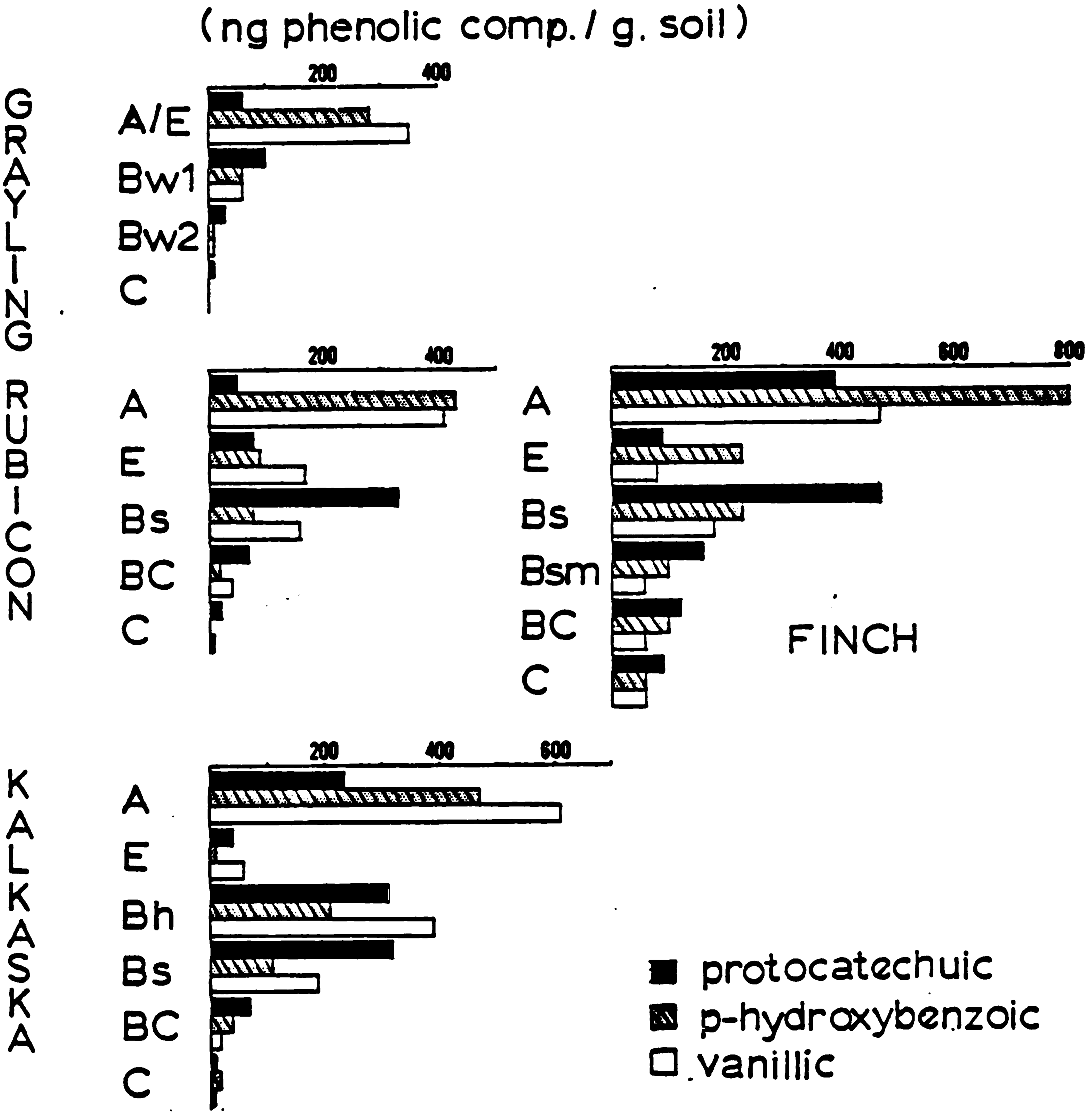


Figure 5. Profile distribution of protocatechuic, p-hydroxybenzoic, and vanillic acids for pedons of study area 3.

depth to water table decreases and spodic horizon development increases within the pedons of the hydrosequences and developmental sequences, respectively. With increased soil moisture, higher levels of organic matter generally tends to build up on the forest floor. This may influence the relationship between soil moisture and the higher concentrations of the major phenolic compounds.

Accumulations of protocatechuic acid occurred in B horizons of all pedons except for Grayling 2 which is a poorly developed soil. Rubicon 1 and Grayling 3 had minimal accumulations whereas the other pedons had about four to twenty fold increases from the E to the B horizon. Only in the well developed profiles of Kinross 1, Kalkaska 2, and Kalkaska 3 were there two B horizons with high accumulations of protocatechuic acid. Maple species dominated the overstory vegetation at these three sites. This suggests a possible relationship between protocatechuic acid accumulations and maple tree species may exist. An ortstein sample taken from the Bs2 horizon of Kinross 1 had a protocatechuic acid content equivalent to that of the Bs1 horizon. From this, it appears that concentrations of protocatechuic acid may occur in isolated areas in lower B horizons.

Generally, only pedons with well expressed spodic horizons have accumulations of *p*-hydroxybenzoic and vanillic acids in B horizons (Fig. 5). These pedons include Kinross 1, Rubicon 2, Kalkaska 2, and Kalkaska 3. In the remaining pedons, the amounts of the two acids decrease with depth. There is no relationship in the distribution of *p*-hydroxybenzoic and vanillic acids to that of iron and aluminum except in the pedons with well expressed spodic horizons.

High concentrations of *p*-hydroxybenzoic acid were extracted from

Rubicon 1, Kalkaska 2, and Finch 3 A horizons (Fig 5). In the two well-drained pedons corresponding low concentrations of protocatechuic acid were extracted. The overstory vegetation on the three sites with high p-hydroxybenzoic acid contents are dominated by deciduous tree species. Aspen are predominant at Rubicon 1 and Finch 3, while maple are dominant at Kalkaska 2.

Possible Origins of the Major Phenolic Compounds

The low concentrations of p-hydroxybenzaldehyde, vanillin, trans p-coumaric acid, and ferulic acid suggest minimal involvement of these compounds in the podzolization process. It may be that their rule is more of intermediary than direct for they can be transformed through biological metabolism to form p-hydroxybenzoic and vanillic acids (Ishikawa et al., 1963; Alexander, 1977). White-rot fungi reduced the three carbon side chain of cinnamic acids to one carbon forming aldehydes (Flaig et al., 1875; Alexander, 1977). The aldehydes are capable of being further oxidized to form benzoic acid derivatives. A process similar to this could conceivably occur in Spodosols. Therefore, the amounts of substituted benzoic acids such as p-hydroxybenzoic and vanillic acids would be greater. Both acids have also been found in extractions of lignin containing plants whereas plants void of lignin generally did not yield these acids (Harborne and Simmonds, 1964).

Another explanation for the low concentrations of the aldehydes and cinnamic acids could be the extractant pH. Ferulic and trans p-coumaric acids were reported as having low recoveries except when extracted with 2 M sodium hydroxide at pH 14.3 (Katase, 1979; 1981b). Newby et al. (1980) explained low recoveries on decomposition of substituted cinnamic acids when extracting with an acidic solution, however, Katase (1981b) believes polymerization responsible.

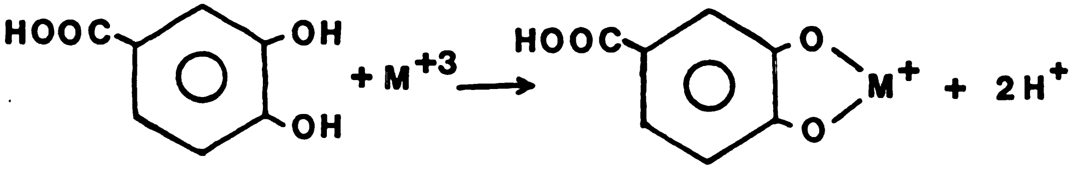
Another source of *p*-hydroxybenzoic and vanillic acids is microbial synthesis. *p*-Hydroxybenzoic acid has been identified in cultures of Epicoccum nigrum (Haider and Martin, 1967), which are fungi of the class Hyphomycetes, a major group of soil fungi (Pritchett, 1979).

There are several potential sources of protocatechuic acid in soils. Chemical and biological degradation of *p*-hydroxybenzoic and vanillic acids has been shown to result in the formation of protocatechuic acid (Shindo and Kuwatsuka, 1975; Haider and Martin, 1975). Conversion of *p*-hydroxybenzoic acid to protocatechuic acid by fungi involved hydroxylation reactions (Alexander, 1977). Demethylation of vanillic acid by white-rot and brown-rot fungi resulted in the formation of protocatechuic acid (Crawford, 1981). Protocatechuic acid is also a constituent of plants and may be formed through microbial metabolism. Carbohydrate metabolism by fungi has been shown to produce protocatechuic acid (Haider and Martin, 1967). The plant species that contain protocatechuic acid belong mainly to the angiosperm class (Harborne and Simmonds, 1964). Although plants contain this acid, the digests of plant lignins has shown no presence of it (Ribereau-Gayon, 1972). This suggests that protocatechuic acid has a different function in plants other than *p*-hydroxybenzoic and vanillic acids, which are both lignin constituents.

Significance of Protocatechuic Acid in the Podzolization Process

Of all the phenolic compounds identified in this study, only protocatechuic acid has ortho dihydroxy functional groups which are capable of forming a chelate complex with polyvalent metal ions such as iron and aluminum. In our studies, protocatechuic acid was observed to accumulate in the B horizons, whereas the other phenolic compounds generally did not. This suggests that protocatechuic acid may be an important pedogenic compound. Many researchers have emphasized the vital role of chelate complexes in bringing into solution metal ions which may otherwise be insoluble (Shindo and Kuwatsuka, 1977; Stevenson, 1983). Weathering processes also rely in part on degradation of soil minerals by soil organic compounds through chelation (Schnitzer, 1978). The solubility of metal ions generally increases when complexed with low molecular weight organic compounds. This allows the downward migration of organo-metallic complexes which may accumulate in subhorizons when conditions render the complexes immobile.

The chelation of protocatechuic acid and metal ions takes place through coordinate bonding between hydroxyl ligand groups and the metal ion, forming a five membered ring structure. Protocatechuic acid has ortho-dihydroxyl functional groups which participate in the chelation reaction in the following manner:



Several properties of the soil environment might affect the above reaction but pH and ionic concentration are the most significant.

Accumulations of protocatechuic acid, iron, and aluminum occurred in B horizons of pedons except for Grayling 2, which is poorly developed (Fig. 5; Table 9). This suggests that protocatechuic acid may have translocated in the form of organo-metallic complexes with Fe and Al and accumulated after being immobilized in the B horizon. The solubility of ferric iron is low at the pH levels found in these soils which means complexation must have occurred in order for iron to have moved. Duchaufour (1982) stated that ferric iron has a low solubility above pH 2.5 and aluminum can exist in exchangeable forms only at low concentrations when pH levels are less than 5. Therefore, these ions probably accumulated by 1) formation of soluble metal-organic complexes in the surface horizons, 2) downward translocation to B horizons, and 3) subsequent immobilization, precipitation, or polymerization.

Protocatechuic acid has been used to elute iron and aluminum from soils (Shindo and Kuwatsuka, 1977). With increased concentrations of protocatechuic acid, more iron and aluminum were eluted. No such relationship was found between concentration and elution by p-hydroxybenzoic acid of iron and aluminum. Adsorption of phenolic acids by subsoil materials was shown to follow the order of protocatechuic > p-hydroxybenzoic > vanillic acids (Shindo and Kuwatsuka, 1976; Vance et al., 1984 (see Chapter 3)). The findings of high concentrations of protocatechuic acid, iron, and aluminum in this study and the results of Shindo and Kuwatsuka (1976, 1977) suggest protocatechuic acid is able to complex iron and aluminum. Once soluble complexes of protocatechuic acid with iron or aluminum are formed, downward translocation through the soil profile can occur. These complexes are immobilized by absorption, polymerization, or precipitation reactions which leads to horizons of accumulation.

SUMMARY AND CONCLUSION

Low molecular weight phenolic compounds were extracted from each horizon of ten soil pedons. There were seven compounds identified in these soils which include three benzoic acids: protocatechuic, *p*-hydroxybenzoic, and vanillic acids; two aldehydes: *p*-hydroxybenzaldehyde and vanillin; and two cinnamic acids: *trans* *p*-coumaric and ferulic acids. The greater portion of the total phenolic compound concentration in each horizon consisted of the substituted benzoic acids. Protocatechuic acid had greater concentrations in the B horizons whereas *p*-hydroxybenzoic and vanillic acids were higher in the A horizons. Low concentration of the aldehydes and cinnamic acids were determined in all horizons with their highest contents in A horizons. *p*-Hydroxybenzoic and vanillic acid accumulate only in spodic horizons of well-developed Spodosols. Protocatechuic acid was found in larger amounts in B horizons as decreased depth to the water and/or increased spodic horizon expression occurred. This trend coincides with pyrophosphate extracted iron and aluminum.

The general implications of these results suggest that phenolic compounds, especially protocatechuic acid and, to a lesser extent, *p*-hydroxybenzoic and vanillic acids, may be involved in the formation of spodic horizons. These compounds have carboxylic and hydroxyl groups that are capable of interacting with iron and aluminum, thus increasing the solubility and mobility of the metal ions. Protocatechuic acid, because of its ability to form chelate complexes and its prevalence in B horizons may play a major role in the podzolization process.

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CHAPTER 5

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

The purpose of this study was to determine if low molecular weight phenolic compounds are involved in the formation of spodic horizons. For this investigation, ten soil pedons representing two hydrosequences and two developmental sequences were sampled. Soil morphological characteristics and vegetation were described at each of the sites. The soils were classified according to soil morphology and tested by three chemical criteria. Low molecular weight phenolic compounds were extracted from the ten soil pedons and their distribution discussed.

Eight of the ten pedons were classified as Spodosols based on morphological characteristics. Chemical analysis indicated that these eight soils had subhorizon accumulations of sodium pyrophosphate extractable iron, aluminum, carbon, and total carbon. The two pedons classified as Entisols showed some accumulations of iron and aluminum in B horizons but not of carbon.

The three chemical criteria for spodic horizons are Soil Taxonomy, Canadian System of Soil Classification, and a new chemical criteria. The B horizons of both Entisols did not meet the criteria of any of the systems. Of the eight pedons classified as Spodosols by morphology alone, only three, Kinross 1, Rubicon 3, and Kalkaska 3, had B horizons which met all three sets of chemical criteria. These three are the only pedons that had spodic horizons according to Soil Taxonomy. The B horizons of two additional pedons, Croswell 1 and Rubicon 2, met the podzolic B horizon (equivalent to the spodic horizon) criteria of the Canadian System. According to the new chemical criteria, all eight pedons with Spodosol morphology had B horizons which met the requirements for the spodic horizon. These results indicate the new chemical criteria have the advantage of correlating morphological characteristics and chemical properties.

Three extractants, sodium hydroxide and sodium pyrophosphate at pH 7 and at pH 10, removed low molecular weight phenolic compounds from horizons of the Kalkaska 3 pedon. Of 28 standard comppunds, only seven were identified in the soil extracts: three carboxylic acids - protocatechuic, *p*-hydroxybenzoic, and vanillic acids; two benzaldehydes - vanillin and *p*-hydroxybenzaldehyde; and two cinnamic acids - *trans* *p*-coumaric and ferulic acids. The amounts extracted were generally greater with higher extractant pH except for protocatechuic acid which was extracted in higher amounts from the Bs, BC, and C horizons by sodium pyrophosphate pH 10. Sodium pyrophosphate pH 7 extracted low concentrations from all horizons. Sodium hydroxide extracted large amounts of all seven phenolic compounds. These large amounts are thought to result from the degradation of organic substances, such as plant residues. Both cinnamic acids were extracted mainly by sodium hydroxide. These compounds are released from plant cell walls thus suggesting their origin is non-pedogenic.

The three most abundant compounds were protocatechuic, *p*-hydroxybenzoic, and vanillic acids. Sodium pyrophosphate pH 10 was the most efficient in the recovery of these three compounds when they were amended to soils and later extracted. Together, the results of the recovery experiment and those of the soil extractions indicate sodium pyrophosphate pH 10 was more specific in removing organic complexes of possible pedogenic nature.

Low molecular weight phenolic compounds were extracted from each horizon of the ten pedons using sodium pyrophosphate pH 10. The seven phenolic compounds extracted in the methodology study were also found in the ten pedons. The three benzoic acids, protocatechuic, p-hydroxybenzoic, and vanillic, made up the majority of the total phenolic compound concentration in each horizon. Vanillic and p-hydroxybenzoic acids accumulated in spodic horizons of only well-developed Spodosols. Protocatechuic acid was found in larger amounts in B horizons as depth to the water table decreased and spodic horizon expression increased. This trend coincided with sodium pyrophosphate extracted iron and aluminum.

Of the seven phenolic compounds, only protocatechuic acid can form chelate complexes with metal ions such as iron and aluminum. The remaining compounds may interact with these metal ions through a weaker complex formation. The general implications of the results of this study suggest protocatechuic acid, iron and aluminum have translocated as organo-metallic complexes which have accumulated in the B horizons. The results also indicate that with greater accumulations of these organo-metallic complexes spodic horizon expression increases.

APPENDIX

Table 11. Site and soil descriptions.

Rubicon 1 (Sandy, mixed, frigid Entic Haplorthod)

Location:	2400 feet west and 500 feet north from the southeast corner of section 17, T.18N., R.6W., Freeman Township, Clare County, Michigan.
Vegetation:	Overstory - 90% quaking aspen (*Populous tremuloides*) 20-30 cm DBH; 10% white pine (*Pinus strobus*) 20-25 cm DBH. Understory - 60% quaking aspen, 40% sugar maple (*Acer saccharum*), black oak (*Quercus velutina*). Ground cover - bracken fern (*Pteridium aquilinum*), ground cedar (*Lycopodium complantatum* and *L. obscurum*), raspberry (*Rubus* sp.), some grasses. Stumps - large white pine.
Oe	2-0 cm; Very dark gray (N 3/0) partially and well decomposed leaves and twigs; many fine roots; strongly acid; abrupt smooth boundary.
A	0-3 cm; Black (10YR 2/1) loamy sand; granular; very friable; many fine and medium roots; extremely acid; clear smooth boundary.
E	3-9cm; Grayish brown (10YR 5/2) sand; single grained; loose; common fine roots; very strongly acid; abrupt wavy boundary.
Bs1	9-35 cm; Dark brown (7.5YR 4/4) loamy sand; subangular blocky; very friable; many fine roots; very strongly acid; clear wavy boundary.
Bs2	35-67 cm; Dark yellowish brown (10YR 4/4) sand; single grained; loose; few fine roots; very strongly acid, gradual wavy boundary.
BC	67-93 cm; Yellowish brown (10YR 5/6) sand; single grained; loose; few fine roots; strongly acid; clear wavy boundary.
C	93-150 cm; Light yellowish brown (10YR 6/4) sand; single grained; loose; very strongly acid.

Sampled by Delbert Mokma and George Vance.

Table 11. Site and soil descriptions.

Croswell 1 (Sandy, mixed, frigid Entic Haplorthod)

Location:	800 feet east and 120 feet south from the west center of section 17, T.18N., R.6W., Freeman Township, Clare County, Michigan.
Vegetation:	Overstory - 60% quaking aspen 15-30 cm DBH, 40% sugar maple 15-30 cm DBH, white birch (*Betula papyrifera*), white pine, northern red oak (*Quercus rubra*). Understory - mainly sugar maple and quaking aspen with some black cherry (*Prunus serotina*) and balsam fir (*Abies balsamea*). Ground cover - bracken fern, blueberry (*Vaccinium* sp.), huckleberry (*Gaylussacia* sp.), ground cedar. Stumps - large white pine.
Oa	4-0 cm; Dark reddish brown (5YR 2/2) leaf litter; many fine roots; very strongly acid; abrupt wavy boundary.
A	0-2 cm; Very dark gray (10YR 3/1) loamy sand; single grained; loose; many fine and medium roots; extremely acid; abrupt irregular boundary.
E	2-7 cm; Pinkish gray (7.5YR 6/2) sand; single grained; loose; common fine and medium roots; extremely acid; abrupt wavy boundary.
Bs1	7-26 cm; Brown (7.5YR 4/4) sand; subangular blocky; very friable; many fine roots; very strongly acid; clear wavy boundary.
Bs2	26-48 cm; Strong brown (7.5YR 5/6) sand; single grained; loose; common fine roots; strongly acid; clear wavy boundary.
BC	48-66 cm; Brownish yellow (10YR 6/6) sand; strong brown (7.5YR 6/6) mottles; single grained; loose; few fine roots; strongly acid; clear wavy boundary.
C1	66-100; Light yellowish brown (10YR 6/4) fine sand; strong brown (7.5YR 5/6) mottles; single grained; loose; strongly acid; clear wavy boundary.
C2	100-125 cm; Light yellowish brown (10YR 6/4) sand; yellowish red (5YR 5/8) mottles; single grained; loose; strongly acid.

Sampled by George Vance and Delbert Mokma.

Table 11. Site and soil descriptions.

Kinross 1 (Sandy, mixed, frigid Typic Haplorthod)

Location:	500 feet south and 125 feet east from the north center of section 15, T.18N., R.6W., Freeman Township, Clare County, Michigan.
Vegetation:	Overstory - 90% sugar maple 10-30 cm DBH, 10% white birch 20-40 cm DBH, white pine 50 cm DBH 80yrs, eastern hemlock (*Tsuga canadensis*). Understory - very sparse consisting mainly of sugar maples. Ground cover - bracken fern, some grasses. Stumps - large white pine.
Oa	9-0 cm; Black (N 2/0) well decomposed leaf litter with some mineral soil material; many fine roots; very strongly acid; abrupt smooth boundary.
A	0-4 cm; Black (10YR 2/1) sand; granular; very friable; many fine and medium roots; extremely acid; abrupt broken boundary.
E	4-19 cm; Light brownish gray (10YR 6/2) sand; single grained; loose; many fine roots; very strongly acid; abrupt wavy boundary.
Bs1	19-32 cm; Dark brown (7.5YR 3/3)sand; reddish brown (5YR 4/4) mottles; subangular blocky; very friable; many fine and medium roots; about 25% strongly cemented concretions and ortstein chunks (2.5YR 2/4); strongly acid; clear wavy boundary.
Bs2	32-51 cm; Brown (7.5YR 4/4) sand; yellowish red (5YR 4/6) mottles; subangular blocky; very friable; many fine roots; bodies of weakly cemented ortstein with mottled (5YR 3/2) interiors; strongly acid; clear wavy boundary.
C	51-73 cm; Yellowish brown (10YR 5/4) sand; dark brown (7.5YR 4/4) and strong brown (7.5YR 5/6) mottles; single grained; loose; strongly acid.

Sampled by Delbert Mokma and George Vance.

Table 11. Site and soil descriptions.

Grayling 2 (Mixed, frigid Typic Udipsamment)

Location:	1800 feet west and 75 feet north from the southeast corner of section 14, T.27N., R.3W., Grayling Township, Crawford County, Michigan.
Vegetation:	Overstory - 95% jack pine (*Pinus banksiana*) 20-30 cm DBH 45-50 yrs, 5% scotch pine (*Pinus sylvestris*). Seedling - northern red oak and white oak (*Quercus alba*). Ground cover - bracken fern, huckleberry, and some grasses and mosses.
Oe	3-0 cm; Very dark grayish brown (10YR 3/2) partially and well decomposed leaf litter; few roots; extremely acid; abrupt smooth boundary.
A/E	0-14 cm; Dark grayish brown (10YR 4/2) and light brownish gray (10YR 6/2) sand; single grained; loose; many fine and medium roots; extremely acid; abrupt wavy boundary.
Bw1	14-45 cm; Strong brown (7.5YR 4/6) sand; single grained; loose; many fine and medium roots; very strongly acid; gradual smooth boundary.
Bw2	45-76 cm; Yellowish brown (10YR 5/6) sand; single grained; loose; many fine roots; strongly acid; clear wavy boundary.
BC	76-93 cm; Light yellowish brown (10YR 6/4) sand; single grained; loose; many fine roots; very strongly acid; clear wavy boundary.
C	93-150 cm; Very pale brown (10YR 7/3) sand; yellowish red (5YR 4/8) mottles; single grained; loose; very strongly acid.

Sampled by Dave Cremeens and George Vance.

Table 11. Site and soil descriptions.

Rubicon 2 (Sandy, mixed frigid Entic Haplorthod)

Location:	150 feet east of west center of section 14, T.27N., R.3W., Grayling Township, Crawford County, Michigan.
Vegetation:	Overstory - 70% red pine (*Pinus resinosa*) 35-45 cm DBH 75-80 yrs, 25% white pine 45-70 cm DBH 65-75 yrs, 5% jack pine. Understory - sugar maple and balsam fir. Ground cover - bracken fern with a distinctive pine needle litter layer
Oe	6-0 cm; Many undecomposed pine needles and black (N 2/0) decay material; many roots; extremely acid; abrupt smooth boundary.
A	0-5 cm; Black (10YR 2/1) sand; granular; very friable; many fine and medium roots; extremely acid; abrupt wavy boundary.
E	5-15 cm; Grayish brown (10YR 5/2) sand: single grained; loose; common fine roots; extremely acid; abrupt wavy boundary.
Bs1	15-31 cm; Reddish brown (5YR 4/4) loamy sand; subangular blocky; very friable; many fine and medium roots; very strongly acid; clear irregular boundary.
Bs2	31-45 cm; Dark brown (7.5YR 4/4) loamy sand; single grained; loose; many fine roots; very strongly acid; abrupt wavy boundary.
BC	45-82 cm; Brown (10YR 5/3) sand; single grained; loose; few fine roots; very strongly acid; clear wavy boundary.
C	82-150 cm; Yellowish brown (10YR 5/4) sand; strong brown (7.5YR 5/4) mottles; single grained; loose; very strongly acid.

Sampled by George Vance and Dave Cremeens.

Table 11. Site and soil descriptions.

Kalkaska Variant 2 (Sandy, mixed, frigid Typic Haplorthod)

Location:	1250 feet north and 150 feet west from the southeast corner of section 6, T.27N., R.3W., Grayling Township, Crawford County, Michigan.
Vegetation:	Overstory - 50% sugar maple 30-40 cm DBH, remaining consisting of quaking aspen 35-45 cm DBH, bigtooth aspen (*Populus grandidentata*) 10-15 cm DBH, white pine 45-50 cm DBH, american beech (*Fagus grandifolia*) 35-40 cm DBH, yellow birch (*Betula lutea*) 30-35 cm DBH, hornbeam (*Ostrya virginiana*) 20-25 cm DBH. Understory - mainly sugar maple with some eastern hemlock. Ground cover and seedlings - bracken fern and sugar maple.
Oe	3-0 cm; Undecomposed leaves and twigs and black (5YR 2/1) decayed materials; many roots; strongly acid; clear smooth boundary.
A	0-6 cm; Very dark gray (10YR 3/1) loamy sand; granular; very friable; many fine and coarse roots; strongly acid; clear wavy boundary.
E	6-12 cm; Grayish brown (10YR 5/2) loamy sand; single grained; loose; many fine roots; very strongly acid; abrupt wavy boundary.
Bh1	12-21 cm; Dark reddish brown (5YR 3/2) sandy loam; subangular blocky; very friable; many fine and medium roots; very strongly acid; clear wavy boundary.
Bh2	21-32 cm; Dark reddish brown (5YR 3/3) sandy loam; subangular blocky; very friable; many fine and medium roots; very strongly acid; abrupt wavy boundary.
Bsm	32-60 cm; Brown (7.5YR 5/4) loamy sand; massive; strongly cemented; very strongly acid; abrupt wavy boundary.
C	60-150 cm; Light yellowish brown (10YR 6/4) sand; single grained; loose; intermittent yellowish brown (10YR 5/4) sand bands; very strongly acid.

Sampled by George Vance and Dave Cremeens.

Table 11. Site and soil descriptions.

Grayling 3 (mixed, frigid Typic Udipsamment)

Location: 2000 feet south and 1150 feet east from the northwest corner of section 26, T.27N., R.8W., Wilson Township, Kalkaska County, Michigan.

Vegetation: Overstory - Sparsely vegetated with 80% jack pine 10-15 cm DBH averaging 6 meter in height, 20% quaking aspen 10-15 cm DBH, red maple (*Acer rubrum*).
Ground cover - blueberry, grasses and mosses.
Stumps - large white pine.

Oa	2-0 cm; Black (N 2/0) well decomposed leaf litter with some undecayed materials; few roots; extremely acid; abrupt smooth boundary.
A/E	0-8 cm; Very dark gray (10YR 3/1) and grayish brown (10YR 5/2) sand; single grained; loose; many fine and common medium roots; extremely acid; abrupt wavy boundary.
Bw1	8-28 cm; Yellowish red (7.5YR 4/6) sand; single grained; loose; common fine roots; strongly acid; gradual wavy boundary.
Bw2	28-54 cm; Yellowish brown (10YR 5/6) sand; single grained; loose; common fine roots; strongly acid; clear wavy boundary.
C	54-150 cm; Light yellowish brown (10YR 6/4) sand; single grained; loose; few fine roots; strongly acid.

Sampled by Dave Cremeens and George Vance.

Table 11. Site and soil descriptions.

Rubicon 3 (Sandy, mixed, frigid Entic Haplorthod)

Location:	1600 feet north and 650 feet west from the southeast corner of section 36, T.30N., R.6W., Star Township, Antrim County, Michigan.
Vegetation:	Overstory - Three large white pine 40-55 cm DBH 90-100 yrs, eastern hemlock 55 cm DBH 120 yrs. Understory - sugar maple and black cherry. Ground cover - bracken fern, thick pine needle forest floor. Stumps - large white pine.
Oe	4-0 cm; Black (N 2/0) partially and well decomposed leaves and twigs; many fine roots; very strongly acid; abrupt smooth boundary.
A	0-6 cm; Black (10YR 2/1) loamy sand; granular; very friable; many fine roots; extremely acid; abrupt wavy boundary.
E	6-21 cm; Brown (7.5YR 5/2) sand; single grained; loose; common medium roots; few chunks of cemented albic material; extremely acid; abrupt wavy boundary.
Bs	21-51 cm; Dark brown (7.5YR 3/4) sand; subangular blocky; very friable; common medium roots; some chunks of cemented material; very strongly acid; clear wavy boundary.
BC	51-86 cm; Yellowish brown (10YR 5/6) sand; single grained; loose; some yellowish red (5YR 4/6) sand bands; common fine roots; very strongly acid; gradual wavy boundary.
C	86-150 cm; Light yellowish brown (10YR 6/6) sand; single grained; loose; discontinuous sand bands 3-10 mm spaced 5-10 cm apart; common fine roots; very strongly acid.

Sampled by George Vance and Dave Cremeens.

Table 11. Site and soil descriptions.

Kalkaska 3 (Sandy, mixed, frigid Typic Haplorthod)

Location: 3600 feet east and 150 feet north from the southwest corner of section 31, T.29N., R.6W., Mancelona Township, Antrim County, Michigan.

Vegetation: Overstory - 50% silver maple (*Acer saccharinum*) 30-35 cm DBH, 40% sugar maple, 10% hornbeam, black cherry.
Understory - bimodal forest consisting mainly of hornbeam 5-6 meter height, some sugar and silver maple.
Ground cover - bracken fern and some grasses.

Oe	5-0 cm; Undecomposed deciduous leaves and black (N 2/0) decayed matter; many fine roots; strongly acid; abrupt smooth boundary.
A	0-9 cm; Black (10YR 2/1) loamy sand; granular; very friable; many fine and medium roots; extremely acid; abrupt smooth boundary.
E	9-23 cm; Grayish brown (10YR 5/2) sand; single grained; loose; common fine roots; extremely acid; clear wavy boundary.
Bh	23-41 cm; Dark reddish brown (5YR 3/2) sand; subangular blocky; very friable; few fine and medium roots; strongly acid; abrupt irregular boundary.
Bs	41-83 cm; Strong brown (7.5YR 4/4) sand; single grained; loose; few fine and medium roots; strongly acid; clear wavy boundary.
BC	83-88 cm; Yellowish brown (10YR 5/4) fine sand; single grained; loose; few fine roots; strongly acid; clear wavy boundary.
C	88-150 cm; Light yellowish brown (10YR 6/4) sand; single grained; loose; strongly acid.

Sampled by George Vance.

Table 11. Site and soil descriptions.

Finch 3 (Sandy, mixed, frigid, ortstein Aeric Haplaquod)

Location:	1850 feet east and 1150 feet north from the southwest corner of section 32, T.31N., R.6W., Jordan Township, Antrim County, Michigan.
Vegetation:	Overstory - 95% bigtooth aspen 5-10 cm DBH, rest consisting of black cherry, sugar maple, white pine 55 cm DBH 70 yrs. Seedlings - sugar maple and black cherry. Ground cover - bracken fern and blueberry. Stumps - large white pine
Oa	5-0 cm; Black (N 2/0) well decomposed leaf litter; many fine roots; very strongly acid; abrupt smooth boundary.
A	0-2 cm; Black (10YR 2/1) sand; granular; very friable; many fine and medium roots; extremely acid; abrupt wavy boundary.
E	2-23 cm; Light brownish gray (10YR 6/2) sand; single grained; loose; many medium roots; extremely acid; abrupt wavy boundary.
Bs	23-35 cm; Yellowish red (5YR 4/6) sand; single grained; loose; some chunks of strongly cemented ortstein; common fine roots; very strongly acid; gradual wavy boundary.
Bsm	35-52 cm; Strongly brown (7.5YR 5/6) sand; red (2.5YR 4/6 and 4/8) mottles; massive; strongly cemented; few chunks of dark reddish brown (5YR 3/4) ortstein; few fine roots; very strongly acid; clear wavy boundary.
BC	52-88 cm; Yellowish brown (10YR 5/4) sand; red (2.5YR 4/6 and 4/8) mottles; single grained; loose; some chunks of cemented materials; very strongly acid; clear wavy boundary.
C	88-101 cm; Yellowish brown (10YR 5/8) sand; single grained; loose; very strongly acid.

Sampled by Dave Cremeens and George Vance.

Table 12 . Particle size analysis of the ten soil pedons.

		Total Soil				Sand					Silt	
Horizon	Textural class	Gravel %	Sand %	Silt %	Clay %	VCS %	CS %	MS %	FS %	VFS %	CSi %	FSi %
Rubicon 1												
A	ls	0.7	84.8	10.4	4.8	1.2	11.8	46.2	23.2	2.5	4.4	6.0
E	s	1.0	86.7	11.4	1.9	1.2	10.8	33.8	38.6	2.3	4.0	7.4
Bs1	ls	3.7	84.7	9.6	5.7	2.1	11.8	42.7	25.6	2.5	5.1	4.5
Bs2	s	8.5	90.5	6.7	2.8	4.0	17.7	48.1	19.5	1.2	3.4	3.3
BC	s	10.2	95.4	3.1	1.5	4.9	20.7	50.4	18.8	0.6	1.6	1.5
C	s	6.8	96.3	2.6	1.1	3.5	13.7	51.5	26.9	0.7	1.0	1.6
Croswell 1												
A	ls	2.3	83.0	12.0	5.0	1.6	11.8	46.6	21.2	1.9	4.2	7.8
E	s	11.8	87.0	10.8	2.2	1.3	9.6	48.2	25.0	2.9	4.8	6.0
Bs1	s	10.7	87.1	8.9	4.0	2.9	9.3	45.2	27.7	2.1	4.3	4.6
Bs2	s	3.0	90.3	7.1	2.6	1.4	8.6	48.5	30.0	1.8	4.5	2.6
BC	s	0.4	95.3	3.2	1.5	0.3	2.7	48.2	42.4	1.8	2.1	1.1
C1	fs	tr	98.1	1.2	0.7	0.1	11.1	21.6	70.3	5.1	1.0	0.2
C2	s	tr	98.9	0.7	0.4	tr	2.2	36.8	57.1	2.7	0.3	0.4

Table 12. Particle size analysis of the ten soil pedons.

Horizon	Textural	Total Soil				Sand					Silt	
		Gravel	Sand	Silt	Clay	VCS	CS	MS	FS	VFS	CSi	FSi
	class	%	%	%	%	%	%	%	%	%	%	%
Kinross 1												
A	s	1.7	88.5	9.2	2.3	0.7	6.6	47.2	31.9	2.2	3.1	6.1
E	s	1.5	92.6	6.3	1.1	0.5	6.3	49.3	33.9	2.7	3.2	3.1
Bs1	s	2.8	89.2	5.0	5.8	1.7	8.4	47.6	29.8	1.8	2.3	2.7
Bs2	s	6.1	90.4	4.2	5.4	1.8	9.2	46.3	31.6	1.4	2.0	2.2
Bs2 ort	s	-	95.2	1.5	3.3	1.2	9.2	57.9	26.2	0.8	0.8	0.7
C	s	0.1	98.9	0.5	0.6	0.1	6.2	66.2	25.7	0.7	0.4	0.1
Grayling 2												
A/E	s	0.6	87.5	9.4	3.1	0.6	11.2	47.0	26.8	1.9	3.9	5.5
Bw1	s	5.4	88.4	8.1	3.5	1.0	9.6	45.0	30.4	2.4	3.9	4.2
Bw2	s	11.3	91.8	6.1	2.1	1.9	10.5	49.0	25.5	4.9	4.0	2.0
BC	s	1.0	98.4	0.8	0.8	0.8	12.9	66.8	17.7	0.2	0.3	0.5
C	s	3.0	98.7	0.6	0.7	0.7	10.6	65.8	21.3	0.3	0.2	0.4
Rubicon 2												
A	s	0.8	90.2	7.5	2.3	0.5	12.5	56.0	19.4	1.9	2.5	4.0
E	s	1.4	88.1	10.7	1.2	0.7	11.4	52.5	21.2	2.3	5.3	5.4
Bs1	ls	5.4	83.3	10.4	6.3	1.0	11.5	47.1	21.8	1.9	4.5	5.9
Bs2	ls	3.8	85.4	9.4	5.2	0.8	11.2	49.8	21.4	2.3	4.8	4.6
BC	s	7.3	95.6	2.7	1.7	2.0	18.4	54.4	20.0	0.8	1.1	1.6
C	s	3.4	97.7	1.1	1.2	0.9	16.0	61.1	19.0	0.6	0.3	0.8

Table 12. Particle size analysis of the ten soil pedons.

		Total Soil				Sand					Silt	
Horizon	Textural class	Gravel %	Sand %	Silt %	Clay %	VCS %	CS %	MS %	FS %	VFS %	CSi %	FSi %
Kalkaska 2												
A	ls	1.7	75.1	21.6	3.3	0.8	13.7	47.3	11.9	1.3	9.8	11.8
E	ls	6.2	74.2	23.4	2.4	0.8	12.8	46.2	12.8	1.6	11.8	11.6
Bh1	sl	3.0	68.4	25.8	5.8	0.8	11.0	41.0	14.2	1.4	12.5	13.3
Bh2	sl	6.3	68.4	26.7	4.9	1.1	10.3	42.3	13.0	1.7	13.8	12.9
Bsm	ls	2.4	74.4	20.7	4.9	0.5	11.2	48.6	13.2	1.0	11.4	9.3
C	s	1.3	96.9	1.9	1.2	0.7	10.4	68.0	17.7	0.2	1.1	0.8
Grayling 3												
A/E	s	1.3	93.0	5.7	1.3	1.1	24.8	57.5	8.9	0.6	2.5	3.2
Bw1	s	1.3	90.5	6.4	3.1	1.1	19.1	56.0	13.5	0.8	2.4	4.0
Bw2	s	6.8	94.6	3.4	2.0	3.2	26.1	49.5	15.2	0.5	1.8	1.6
C	s	12.6	98.0	1.2	0.8	2.2	24.0	61.4	10.3	0.2	0.4	0.8
Rubicon 3												
A	ls	2.8	86.7	10.5	2.8	1.4	15.0	48.9	19.3	2.1	4.4	6.1
E	s	7.1	89.1	9.4	1.5	1.3	11.2	48.2	25.5	2.9	4.0	5.4
Bs	s	18.5	92.4	5.3	2.3	2.6	12.5	49.9	25.2	2.2	2.3	3.0
BC	s	1.2	96.2	2.4	1.4	1.4	11.5	44.2	34.0	5.2	1.7	0.7
C	s	2.0	98.3	0.8	0.9	0.8	10.0	60.8	25.9	0.7	0.2	0.6

Table 12. Particle size analysis of the ten soil pedons.

		Total Soil				Sand					Silt	
Horizon	Textural class	Gravel %	Sand %	Silt %	Clay %	VCS %	CS %	MS %	FS %	VFS %	CSi %	FSi %
Kalkaska 3												
A	ls	0.5	85.0	11.7	3.3	1.0	17.0	52.0	14.3	0.7	4.6	7.1
E	s	2.4	90.1	8.3	1.6	1.0	15.6	48.4	24.3	0.8	3.2	5.1
Bh	s	4.0	91.0	5.9	3.1	1.9	16.8	49.2	22.6	0.4	2.5	3.4
Bs	s	7.3	97.6	1.2	1.2	1.6	18.4	61.2	15.9	0.4	0.5	0.7
BC	fs	0.2	98.8	0.8	0.4	0.2	2.4	40.3	55.0	1.0	0.5	0.3
C	s	0.2	99.1	0.5	0.4	0.3	8.9	63.2	26.2	0.4	0.3	0.2
Finch 3												
A	s	0.6	89.9	7.8	2.3	1.0	17.0	54.1	17.0	0.9	2.7	5.1
E	s	1.5	92.8	5.7	1.5	1.3	15.4	57.8	17.3	1.0	2.1	3.6
Bs	s	4.6	94.3	2.0	3.7	3.4	19.4	57.1	14.0	0.4	0.6	1.4
Bsm	s	0.6	96.4	0.2	2.6	0.7	6.9	43.2	43.2	2.3	0.6	0.4
BC	s	1.7	98.9	0.1	1.0	1.2	12.4	63.6	21.4	0.3	0.0	0.1
C	s	0.2	98.8	0.1	1.1	0.2	8.2	57.1	32.5	0.7	0.0	0.1

Table 13. Chemical properties of the ten soil pedons.

Horizon	pH H_2O	pH $CaCl_2$	CEC	Base Saturation K	Base Saturation Mg	Base Saturation Ca	Na Dit-Cit Fe	Na Dit-Cit Al	Na Pyrophosphate Fe	Na Pyrophosphate Al	Na Pyrophosphate C	Total C	Oxidizable C
			--------meq/100g------				%	%	%	%	%	%	%
Rubicon 1													
A	4.3	3.7	8.0	0.1	0.3	1.7	0.18	0.03	0.04	0.04	-	5.52	1.24
E	4.6	3.7	2.9	tr	0.1	0.5	0.18	0.02	0.04	0.02	0.39	0.89	0.38
Bs1	4.9	4.3	7.1	tr	tr	0.6	0.46	0.18	0.18	0.16	0.83	1.09	0.49
Bs2	4.9	4.4	4.1	tr	tr	0.3	0.26	0.10	0.05	0.09	0.42	0.52	0.20
BC	5.2	4.6	1.8	tr	0	0.3	0.16	0.06	0.04	0.06	-	0.23	0.10
Croswell 1													
A	3.9	3.0	11.0	0.1	0.2	1.0	0.12	0.03	0.04	0.03	-	6.09	1.78
E	4.0	3.4	3.0	tr	0.1	0.6	0.12	0.01	0.02	0.01	0.31	1.09	0.45
Bs1	5.0	4.5	9.3	tr	tr	0.5	0.44	0.40	0.10	0.25	0.81	2.28	0.72
Bs2	5.1	4.6	3.2	tr	tr	0.5	0.31	0.19	0.08	0.11	0.39	0.66	0.24
BC	5.1	4.6	1.6	tr	tr	0.4	0.20	0.09	0.06	0.08	-	0.23	0.11
C1	5.1	4.6	1.3	tr	0	0.3	0.12	0.05	0.05	0.06	-	0.10	0.08
C2	5.1	4.6	0.8	tr	tr	0.3	0.26	0.04	0.06	0.04	-	0.09	0.05
Kinross 1													
A	3.8	3.0	13.4	0.2	0.5	2.4	0.11	0.06	0.04	0.04	-	13.10	1.47
E	4.5	3.6	1.9	tr	0.1	0.5	0.6	0.1	0.1	0.1	0.29	0.99	0.29
Bs1	5.1	4.3	27.8	0.1	0.2	1.2	1.40	0.92	0.86	0.58	2.76	8.76	2.49
Bs2	5.2	4.6	22.0	tr	tr	0.4	0.66	0.95	0.19	0.40	1.33	4.98	1.33
Bs2ort	5.1	4.4	21.1	-	-	-	0.27	0.74	0.11	0.47	1.64	7.39	1.54
C	5.2	4.5	1.3	tr	0	0.2	0.07	0.05	0.02	0.06	-	0.16	0.12

Table 13. Chemical properties of the ten soil pedons.

	pH		CEC	Base Saturation			Na Dit-Cit		Na Pyrophosphate			Total	Oxidizable
Horizon	H_2O	$CaCl_2$		K	Mg	Ca	Fe	Al	Fe	Al	C	C	C
			-----meq/100g-------				%	%	%	%	%	%	%
Grayling 2													
A/E	4.3	3.7	7.7	0.1	0.1	0.6	0.34	0.08	0.10	0.07	0.96	8.39	1.21
Bw1	4.8	4.5	4.2	0	tr	0.3	0.26	0.14	0.06	0.14	0.43	1.02	0.34
Bw2	4.9	4.6	2.2	tr	tr	0.8	0.40	0.07	0.04	0.08	0.34	0.31	0.10
BC	4.9	4.7	1.3	tr	tr	0.9	0.06	0.03	0.02	0.04	-	0.27	0.06
C	4.9	4.7	1.4	tr	tr	0.8	0.06	0.02	0.01	0.03	-	0.20	0.01
Rubicon 2													
A	3.9	3.2	16.8	0.2	0.3	1.9	0.03	0.03	0.02	0.02	-	14.87	1.87
E	4.3	3.5	4.0	tr	tr	1.1	0.01	0.01	0.01	0.01	0.35	1.09	0.26
Bs1	4.7	4.3	17.8	0.1	tr	0.7	0.66	0.56	0.20	0.28	1.21	4.37	1.09
Bs2	4.5	4.3	10.3	0.1	tr	0.4	0.28	0.22	0.06	0.14	0.40	1.01	0.38
BC	4.5	4.4	2.0	tr	tr	1.1	0.03	0.04	0.03	0.06	-	0.29	0.08
C	4.7	4.5	1.7	tr	tr	0.8	0.01	0.02	0.01	0.02	-	0.36	0.14
Kalkaska 2													
A	5.4	5.1	22.3	0.2	0.8	7.6	0.13	0.02	0.04	0.02	-	11.89	4.07
E	4.7	3.9	10.9	0.1	0.1	1.1	0.12	0.01	0.02	0.01	0.64	1.17	0.50
Bh1	4.8	4.1	19.2	0.1	0.2	1.4	0.74	0.18	0.36	0.14	1.60	2.75	1.04
Bh2	4.8	4.2	25.7	0.1	0.1	0.6	0.52	0.24	0.22	0.20	1.22	2.90	0.98
Bsm	5.0	4.3	7.5	0.1	0.1	0.5	0.30	0.10	0.05	0.08	0.41	0.62	0.21
C	5.0	4.4	1.9	tr	tr	0.3	0.11	0.03	0.02	0.03	-	0.39	0.12

Table 13. Chemical properties of the ten soil pedons.

	pH		CEC	Base Saturation			Na Dit-Cit		Na Pyrophosphate			Total	Oxidizable
Horizon	H_2O	$CaCl_2$		K	Mg	Ca	Fe	Al	Fe	Al	C	C	C
			-----meq/100g-------				%	%	%	%	%	%	%
Grayling 3													
A/E	4.0	3.3	10.3	0.1	0.1	0.7	0.08	0.04	0.06	0.04	0.93	16.31	2.25
Bw1	5.2	4.6	6.7	tr	tr	0.4	0.30	0.20	0.12	0.18	0.47	1.16	0.41
Bw2	5.3	4.9	3.2	0.1	tr	0.4	0.12	0.08	0.04	0.08	0.23	0.42	0.14
C	5.4	4.9	1.5	0.1	tr	0.4	0.07	0.03	0.02	0.03	-	0.32	0.08
Rubicon 3													
A	4.4	4.2	13.9	0.2	0.6	3.4	0.14	0.02	0.02	0.02	-	14.31	3.28
E	4.2	3.6	3.0	tr	0.1	0.5	0.16	0.02	0.04	0.02	0.44	1.04	0.42
Bs	4.6	4.2	8.1	tr	tr	0.3	0.41	0.29	0.16	0.22	1.00	1.46	0.72
BC	4.8	4.4	2.4	tr	tr	0.3	0.13	0.12	0.04	0.10	-	0.41	0.21
C	4.9	4.5	1.0	tr	tr	0.3	0.07	0.04	0.02	0.04	-	0.31	0.08
Kalkaska 3													
A	4.3	3.8	8.4	0.2	0.6	4.2	0.16	0.04	0.05	0.03	-	4.32	4.66
E	4.2	3.5	6.6	tr	0.1	0.6	0.08	0.02	0.04	0.02	0.58	0.64	0.41
Bh	4.9	4.1	11.7	0.1	tr	0.5	0.33	0.22	0.17	0.18	0.99	1.43	1.06
Bs	5.1	4.5	2.7	tr	0	0.3	0.09	0.11	0.04	0.11	0.49	1.36	0.24
BC	5.1	4.6	2.4	tr	0	0.3	0.12	0.08	0.03	0.08	-	0.49	0.14
C	5.1	4.6	1.9	tr	0	0.3	0.05	0.04	0.02	0.04	-	0.38	0.09

Table 13. Chemical properties of the ten soil pedons.

	pH		CEC	Base Saturation			Na Dit-Cit		Na Pyrophosphate			Total	Oxidizable
Horizon	H_2O	$CaCl_2$		K	Mg	Ca	Fe	Al	Fe	Al	C	C	C
			------meq/100g------				%	%	%	%	%	%	%
Finch 3													
A	4.2	3.6	10.1	0.5	0.4	2.0	0.10	0.02	0.02	0.02	-	11.40	2.13
E	4.2	3.4	0.9	tr	tr	0.5	0.07	tr	0.01	0.02	0.22	0.78	0.16
Bs	4.7	4.4	6.2	tr	tr	0.4	0.28	0.26	0.12	0.22	0.71	2.05	0.38
Bsm	4.9	4.6	6.2	tr	0	0.4	0.26	0.34	0.10	0.22	0.78	0.88	0.26
BC	4.7	4.5	1.7	tr	0	0.4	0.05	0.09	0.01	0.10	0.32	0.43	0.22
C	4.7	4.4	1.3	tr	tr	0.3	0.05	0.08	0.01	0.08	-	0.38	0.10

Table 14. Percent elemental and oxide forms of potassium, calcium, magnesium, iron and aluminum in soil parent materials by total digestion with hydrofluoric acid. (oxides are listed in parenthesis)

SITE & HORIZON	K	Ca	Mg	Fe	Al	TOTALS
	%					
RUBICON 1						
C	1.02(1.22)	0.21(0.29)	0.14(0.23)	0.73(1.04)	2.67(5.05)	4.77(7.83)
CROSWELL 1						
C1	1.07(1.28)	0.27(0.37)	0.11(0.19)	0.94(1.35)	2.51(4.75)	4.90(7.94)
C2	0.84(1.01)	0.19(0.27)	0.09(0.14)	1.12(1.61)	1.94(3.66)	4.18(6.69)
KINROSS 1						
C	0.93(1.11)	0.13(0.19)	0.08(0.14)	0.38(0.54)	2.20(4.15)	3.72(6.12)
GRAYLING 2						
C	0.65(0.78)	0.06(0.09)	0.04(0.07)	0.32(0.45)	1.28(2.42)	2.35(3.81)
RUBICON 2						
C	0.79(0.94)	0.08(0.11)	0.06(0.10)	0.37(0.53)	1.64(3.10)	2.94(4.78)
KALKASKA 2						
C	0.68(0.81)	0.07(0.10)	0.05(0.08)	0.45(0.64)	1.38(2.60)	2.63(4.24)
GRAYLING 3						
C	0.71(0.85)	0.05(0.07)	0.05(0.08)	0.34(0.49)	1.35(2.54)	2.50(4.03)
RUBICON 3						
C	0.89(1.07)	0.08(0.11)	0.05(0.08)	0.31(0.45)	1.71(3.22)	3.04(4.92)
KALKASKA 3						
C	0.68(0.82)	0.06(0.09)	0.04(0.06)	0.13(0.49)	1.48(2.79)	2.61(4.25)
FINCH 3						
C	0.89(1.07)	0.07(0.09)	0.04(0.06)	0.24(0.35)	1.75(3.30)	2.99(4.87)

Table 15. Kalkaska-3 phenolic compounds and standard deviations when extracted by three extractants.[a]

Horizon	Protocatechuic acid	p-Hydroxybenzoic acid	Vanillic acid	p-Hydroxybenzaldehyde	Vanillin	trans-p-Coumaric acid	Ferulic acid	TOTAL
PYROPHOSPHATE (7)								
A	155(30)	157(20)	190(28)	14(1)	18	0	0	534
E	16(2)	0	28(4)	0	0	0	0	44
Bh	63(10)	76(9)	124(3)	6(1)	tr	0	0	269
Bs	86(16)	32(2)	82(9)	6(1)	6	0	0	211
BC	6(4)	14(4)	9(4)	tr	tr	0	0	29
C	0	0	0	0	0	0	0	0
PYROPHOSPHATE (10)								
A	233(11)	468(14)	612(37)	14(1)	52(1)	29(3)	42	1450
E	36(5)	11(6)	64(2)	5(1)	12(4)	0	0	128
Bh	308(21)	209(51)	390(58)	27(3)	30(1)	tr	tr	964
Bs	324(25)	113(4)	191(18)	26(0)	37(4)	0	0	691
BC	71(1)	38(4)	24(1)	5(1)	10(2)	0	0	141
C	6(2)	15(3)	8(2)	2(1)	8(1)	0	0	31
NaOH								
A	2096(76)	2780(168)	3436(363)	1224(158)	1580(115)	824(88)	576(70)	12520
E	164(12)	199(21)	284(6)	108(1)	120(4)	44(0)	116(32)	1093
Bh	593(31)	734(21)	1331(38)	276(4)	408(58)	143(10)	318(1)	3623
Bs	608(40)	432(23)	696(56)	131(8)	170(13)	90(3)	175(23)	2303
BC	54(23)	110(1)	104(4)	15(0)	32(1)	0	0	315
C	0	41(10)	28(1)	8(5)	18(1)	0	0	95

[a] Data expressed in ng phenolic compound/g soil. Standard deviations in parenthesis.

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