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REFORMATION OF CRUSHED ORTSTEIN AND

PODZOLIZATION IN A PIT IN MICHIGAN

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Carol Jean Bronick

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Delbert L. Mokma
Major professor

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REFORMATION OF CRUSHED ORTSTEIN AND PODZOLIZATION IN A PIT IN MICHIGAN

By

Carol Jean Bronick

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ABSTRACT

REFORMATION OF CRUSHED ORTSTEIN AND PODZOLIZATION IN A SOIL PIT IN MICHIGAN

By

Carol Jean Bronick

Blueberries in isolated regions of fields in Michigan experience reduced growth, possibly a result of ortstein development. Growers have attempted deep tillage and a soil amendment to reduce ortstein in these regions with only temporary benefits. This study was conducted to assess if crushed ortstein would recement, the rate, degree and strength of recementation, the nature of the cementing agents, the effect of podzolizing species, depodzolizing species, leaf decomposition and a soil amendment in the recementation. Crushed ortstein from Saugatuck sand (Typic Durorthod, sandy, mixed, mesic) was passed through a 2 mm sieve and used in column experiments to assess recementing. Aqueous extracts of green and brown blueberry leaves, podzolizer and depodzolizer leaves were added to crushed ortstein columns. The degree and strength of aggregation were assessed by determining the amount of treated ortstein remaining on a 2 mm sieve and by tensile strength analysis of aggregated material. Ammonium oxalate extracts and direct coupled plasma were used to assess Al and Fe distribution in treated crushed ortstein. Changes in organic matter (OM), Al, Fe, color and pH were assessed as well as changes in weight and strength of the ortstein pieces. Recementation of crushed ortstein began within 1½ weeks. Degree and strength of cementation tended to increase with duration of the experiment and in the upper layers in the column. Aggregated materials in the lower layers contained higher Al and lower C. OM appear to have been the primary

cementing agent in the upper layers and Al-containing compounds in the lower layers. Podzolizer treatments and green blueberry leaf extracts had lower pH, greater aggregation, stronger aggregates and increased translocation of Al than depodzolizing treatments and brown blueberry leaf extract. Ortstein pieces treated with leaf extract from depodzolizing species or Symbex tended to have decreased weight and/or strength. Depodzolizing species and Super Symbex 4X along with deep tillage may inhibit the recementation of ortstein in blueberry fields.

The ability of selected organic acids to aggregate crushed ortstein and the effect of adding a commercial soil amendment, Super Symbex 4X, were assessed. Solutions of protocatechuic acid (PCA), ρ-hydroxybenzoic acid (ρHBA), catechol and vanillic acid (VA) with and without Symbex, were added to crushed ortstein. After 5 weeks the mixtures had visible changes in color, aggregation and microbial activity. The water control and catechol did not show high levels of aggregation. PCA, ρHBA and VA showed high levels of aggregation. Addition of Super Symbex 4X decreased aggregation with the strongly aggregating organic acids while increasing weakly aggregating solutions.

A pit resulting from removal of soil material for highway construction, was studied to evaluate how quickly evidence of podzolization was apparent. The purpose of this study was to assess podzolization under Jack pine and Red pine planted on C horizon material and compare the effect of these tree species to barren parent material. E, B and C horizon materials were analyzed for OM, Al and Fe, pH and color. Soil colors, OM, pH, Al and Fe show evidence of podzolization after approximately 40 years of soil formation.

To

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for all their love and support

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Reformation of Crushed Ortstein and Podzolization in a Soil Pit in Michigan

Introduction

The North American production of blueberries in 2001 was estimated at over 200 million pounds. The blueberry market is growing rapidly as appreciation for the nutritious value of blueberries increases. Blueberries are a natural source of fiber, vitamin C and antioxidants. Anthocyanins, the blue pigment in blueberries, has been associated with improved eye-sight and blueberry consumption has been associated with reduced aging problems and lower blood pressure. Bacterial inhibitors contained in blueberries have been suggested to reduce urinary infections. Blueberries also contain citric, folic, ellagic a, p-coumaric, caffeic, citric and ferulic acids (North American Blueberry Council, 2001).

Michigan is the nations largest producer (40%) of cultivated highbush blueberries (*V. corymbosum* L.), producing over 72 million pounds in 2000 (Michigan Department of Agriculture, 2000). Blueberry production in Michigan is located in the southwestern and west central portion of the Lower Peninsula, with about 17,000 acres in production. The farm-level value of blueberries in Michigan was over $57 million in 1999, making blueberries the second highest valued fruit crop in Michigan (Michigan Department of Agriculture, 2000). The Michigan blueberry yield in 1999 was 4,340 pounds per acre. The 1999 wholesale price per pound of fresh blueberries was 79 cents, averaging over $3000 per acre.

Issue

Blueberry growers in southwest Michigan have experienced diminished growth in some blueberry replants. This occurs in isolated regions of fields, in which the remainder of the replants have reached full size and production. Blueberries are grown primarily on Spodosols such as the Saugatuck sand (Typic Durorthod, sandy, mixed, mesic) which has a well-developed Bhsm (ortstein) horizon at about 8-20 inches, generally >10 inches thick. The ortstein, commonly called hardpan, varies in occurrence and thickness within the fields. Ortstein has been reported to reduce blueberry growth (Lilly et al., 1975). It has been suggested that the ortstein layer acts as a barrier to water and root penetration. Growers have attempted to break up the ortstein layer with deep tillage prior to replanting blueberries. This has not been a permanent solution. Some growers have come to believe that the ortstein has reformed (Vern Brower, 1999, personal communication). One grower physically removed the ortstein from a field and replaced it with uncemented sand and is considering removing the ortstein from a second field. Other growers are considering removing the producing blueberries, deep tilling to break the ortstein and planting new bushes.

The costs associated with breaking up or removing ortstein, replanting, waiting several years until the plants begin production are a significant financial investment for growers. Plants that do not develop well along with large areas out of production represent a sizeable financial loss to growers. Additional costs from subsoiling and soil amendments in attempts to overcome the problem further add to the loss. Deep tillage may represent only a temporary solution to the problem. One concern is whether the deep tillage fully penetrated the ortstein layer. It is not known if disturbed ortstein will recement, and if so, how quickly this can occur. Concerns over the reformation of spodic hardpans after disturbance have been mentioned in the literature (Wells and Northey, 1985), however there has been no follow up.

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CHAPTER 1

LITURATURE REVIEW

Blueberries

Blueberries belong to the genus *Vaccinium*, a member of the *Ericaceae* (heath) family, Order Ericales (Haffner, 1993). In Michigan *V. corymbosum* L. (highbush) are cultivated. In regions of North America other taxa of *Vaccinium* are grown; *V. ashei* Reade (Rabbiteye), *V. myrtilloides* Michx. (velvet leaf), and *V. augustifolium* Ait. (lowbush) are commercially produced (Hancock and Draper, 1989). Hybrid highbush varieties in Michigan include Bluecrop, Jersey, Rubel and Elliot (Jess, 1999). Blueberries and other *Vaccinium* (cranberry, lingonberry, bilberry) are grown in subtropical, temperate and boreal regions including North America, Europe, Australia, New Zealand and Asia (Haffner, 1993).

Blueberries tend to grow naturally in regions of low soil nutrient status, and are unusual in their preference for acidic soil and ability to utilize nitrogen in the ammonium rather than the nitrate form. Blueberries prefer sandy, acidic (pH of 3.5 to 5.5), well-drained, porous soil with a high organic content and adequate aeration (Hancock and Draper, 1989; Hanson and Retamales, 1992; Haffner, 1993). Blueberries require 160 growing days along with a low temperature period to meet chill requirements of 650-850 hours below 7°C (Haffner, 1993). Highbush blueberries are adapted to lowland, acid soil (Eck, 1988) and produce aromatic, large berries compared to wild types (Haffner, 1993). Highbush blueberries tend to be more winter-hardy and require more chilling hours than rabbiteye.

Blueberries are shallow rooted and lack root hairs (Haffner, 1993). The fibrous, diffuse root system rarely extends beyond the drip line (Eck, 1988). Fine lateral roots are sometimes considered root hairs. The thickness of the topsoil layer determines root depth and root growth can be stimulated by shallow cultivation (Eck, 1988; Goulart et al., 1993). The limited root system tends to make blueberries susceptible to aeration and moisture stresses levels; both drought and standing water can cause damage (Haffner, 1993). The root systems have a symbiotic relationship with mycorrhizal fungi that assist the blueberries in nutrient uptake, however, excess minerals in the soil water can damage blueberry roots (Haffner, 1993) and inhibit development of mycorrhizae (Goulart et al., 1993).

Plants require approximately 25-50 mm of rainfall weekly during the growing season (Haffner, 1993). Moisture requirements are often met through supplemental irrigation in Michigan. In Michigan, shallow aquifer irrigation tends to supply water with a low pH and high Fe content, while deeper aquifer irrigation water is alkaline (Hanson, 2000, personal communication).

Propagation occurs via hardwood cuttings spaced 1.2 to 1.5 m apart in rows, rows placed 2.4 to 3.0 m apart (Hancock and Draper, 1989). Plants are maintained at a height of 1.8 to 2.5 meters, although they can grow to 4.0 meters (Hancock and Draper, 1989). Blueberry bushes produce for more than 20 years, after an initial few years of no production (Michigan Agricultural Statistics, 1997-1998).

Cover crops of spring oats and Sudan grass are frequently used in Michigan; manure and leguminous mulch can be detrimental to blueberries (Eck, 1988). In some circumstances an accumulation of organic matter on the soil surface can reduce aeration sufficiently to reduce growth (Haffner, 1993). Cover crops allow "for the timely hardening of blueberry plants in the fall that decreases susceptibility to winter injury" possibly by limiting nitrogen availability late in the season (Eck, 1988). Herbicides are used to control weed growth under bushes. A single application of ammonium sulfate or urea is common in Michigan. Sod strips between rows are common (Hancock and Draper, 1989), although sod may increase difficulty in controlling mummy berry disease.

Spodosols

"Spodosols are the dominant soil order in Michigan" (Mokma, 1991) and are naturally acidic and sandy, some have seasonally high water tables. These conditions are favorable to blueberries. Spodosols have a spodic horizon or podzol B horizon (SSSA, 1997). Soil Taxonomy (Soil Survey Staff, 1975) states that spodic material, an essential component of the spodic horizon and Spodosols, must have a pH in water of ≤ 5.9 and an organic C content $\geq 0.6\%$. In addition, it must have one or more of the following: reddish or dark colors, cementation, coated sand grains, optical density color of oxalate extract, or certain Fe and Al contents of oxalate extract (Lundström et al., 2000). The spodic horizon commonly underlies a light-colored, eluvial zone comprised of an A horizon and an albic E horizon (Mokma and Buurman, 1982). The C horizon beneath the illuvial spodic horizon generally exhibits minimal indications of soil formation (Lundström et al., 2000).

Detailed reviews of podzols and podzolization have been compiled by Mokma and Buurman (1982), Lundström et al. (2000) and others. Podzolization requires the mobilization of organic compounds and sesquioxides in the eluvial zone along with their transport and deposition in the illuvial zone. Prior to the mobilization of organics, soluble salts and bases have leached from the upper horizons (Mokma and Buurman, 1982). The amounts of Al and Fe in the spodic horizons increase with time. Cemented, hardpan layers can develop, forming ortstein. DeConinck (1980) concluded that ortstein formation occurred when the supply of organo-metallic compounds in the illuvial horizons exceeds the biological activity to decompose organic ligands. Immogolite, Al, Fe and carbon have been identified as cementing agents in ortstein. Al-complexed organic matter has been identified as the cementing agent in podzols in Florida (Lee et al., 1988a), France (Righi and DeConinck, 1977) and Canada (Miles, 1978; McKeague and Wang, 1980). The rate of translocation of C, Al and Fe has been investigated in several chronosequences of Spodosols or Podzols with the focus on the spodic horizon or the albic horizon. Often these studies have not evaluated young profiles or assessed the chemical properties of podzolization (Mokma and Yli-Halla, 2001). These studies have determined that the development of typical Spodosol horizonation commonly occurs in excess of 500 years while a visible profile can be apparent in 75-120 years in some environments.

Spodosols commonly occur in temperate regions of America, Europe and Asia (Lundström, 2000) comprising 2.5% of the ice-free land surface (Evans and Mokma, 1996). They are less common in humid tropics, tundra and polar regions (Lundström et al., 2000). Due to drier conditions and warmer winter temperatures Spodosols are also less common in the southern hemisphere (Lundström et al., 2000). "In Michigan ortstein tends to form in somewhat poorly drained soils" (Mokma, 1991).

Spodosol Development

The formation of Spodosols is generally favored by cool, moist climates and coarse-textured soils. "Podzols are typically found on coarsely textured, base-poor parent materials such as sands and sandy tills," (Lundström et al., 2000). The five soil-forming factors; climate, parent material, time, topography and vegetation along with their interaction, determine the degree and type of soil formed. Spodosol development requires that precipitation exceed evaporation. Spodosols do not occur in arid environments (Mokma and Buurman, 1982). Soil temperatures are not important in the development of Spodosols, although in cooler climates spodic horizons tend to be shallower than in warm climates (Mokma and Buurman, 1982; Schaetzl and Isard, 1996).

The rate of Spodosol development is highly variable, depending on the soil forming factors. The chemical properties of upper horizons can reflect changes in vegetation in a matter of years while soil physical properties and profile changes are apparent in decades. Soil pH and base content are early indicators of chemical changes due to plant induced acidification and translocation of materials (Miles, 1985a). Such changes have been reported in as short a time as 3 years (Bollen et al., 1969, from Miles, 1985a). Changes in physical properties such as color, horizonation, porosity, structure, and cementation can be apparent in decades, changes have been reported in 18 years (Miles, 1985a). Changes in soil profiles following changes in vegetation have been observed in 50-60 years (Nornberg et al., 1993). The time required for the formation of a fully developed podzolic profile can range from 350 to 10,000 years.

The Role of Vegetation in Spodosol Formation

Vegetation induced changes in soils, which impact plant growth, have been noted in the literature (Miles, 1985b). The role of vegetation in the podzolization process has been well established (Dimbleby and Gill, 1955; Mokma and Buurman, 1982; Nornberg et al., 1993; Willis et al., 1997; van Breemen et al., 2000). It has been widely noted that vegetation affects podzolization development and rates as well as depodzolization (Mokma and Buurman, 1982; Nornberg et al., 1993; Willis et al., 1997; van Breemen et al., 2000). Some acidifying plants such as kauri, white pine, ericaceous shrubs (including blueberries), hemlock and spruce are podzolizers (Dimbleby and Gill, 1955; Miles, 1985a; Mokma and Buurman, 1982). Oak, birch, fescue-bent grass and bracken fern have been noted to decrease podzolization and are considered ameliorating plants (Nornberg et al., 1993; Miles, 1985a).

In cool climates Spodosol formation is favored by coniferous forest and heath vegetation (Mokma and Buurman, 1982; Lundström et al., 2000). In warmer regions Spodosols tend to form under savannah, palms and mixed forest (Mokma and Buurman, 1982).

Changes in soil acidity and podzolization as a result of the natural cycling of vegetation and successional events such as burning and grazing are described by Mokma (1991) and Miles (1885a). The organic matter accumulation and organic acids and their ability to complex Al and Fe vary with vegetation type (Mokma, 1991). The rate of decomposition, nutrient recycling and ability to "acidify the soil and accelerate eluviation" also vary, affecting the rate of soil alterations (Duchaufour, 1982 from Miles, 1985a). Detectable signs of depodzolization have been reported in 18 years after birch, a depodzolizer, replaced heather, a podzolizer (Miles, 1978). He reported "substantial changes in soil color, organic matter content, porosity, structure and cementation." Soil changes and depodzolizing trends in soils were reported within decades of replacing heath with oak (Nielsen et al., 1999).

"Plant-induced changes in soil" were described by Miles (1985a). The chemical composition of plant materials, rate of decomposition and decomposition products differ, affecting eluviation processes in soils. This is particularly true of long-lived species. The chemical properties, such as pH, of upper horizons can reflect changes in vegetation in a matter of years while soil physical properties and profile changes are apparent in decades. Changes in soil profiles following changes in vegetation have been observed in 50-60 years (Nornberg et al., 1993).

A long-term, dynamic equilibrium that exists between contrasting plant species naturally "inhibits the development of strongly podzolized soils" (Miles, 1985a). This cyclical relationship between heather and bracken fern has been disturbed by management practices that maintain heather. It has been noted that as bracken fern encroached on heather it caused a "change in humus type and distribution" as well as "some redistribution of sesquioxides in the soil" (Jarvis and Duncan, 1976). Such cycles have been reported elsewhere between pine and birch and heather and birch.

Ericaceous species are generally associated with soil acidification and podzolization (Miles, 1985a). He also reported that bracken fern (*Pteridium aquilinum*) and bent-fescue (*Agrostis-Festuca*) tend to reduce acidity and depodzolize soil. Bracken fern is a common associate of *Vaccinium* in natural systems (Swink, 1994). In natural systems blueberries and ericaceous plants are commonly associated with oak trees and bracken ferns. These plants compliment the podzolizing effect of the ericoids with depodzoling effects, forming a dynamic equilibrium (Miles, 1985a). The vegetation-induced changes are considered to be reversible.

The development of Spodosols has been linked to the influence of surface litter (Wells and Northey, 1985; Mokma, 1991). It has been suggested that organic acids released from blueberry leaf litter as it is broken down, complex with Al and Fe transporting them downward. Microbial degradation of the organic ligands causes the precipitation of Al and Fe. The primary acid believed to participate in this translocation process in Michigan Spodosols is protocatechuic acid, which paralleled the distribution of Al and Fe in the soil profile (Vance et al., 1986).

It has been proposed that Al and Fe are released from the parent material by weathering and complexed to organic acids (Lundström, 2000). The soluble, organo-metallic complexes are transported down the soil profile. "Organic acids in soils could be produced by leaching from plants, decomposition of litter by microbes and exudation by roots, fungi and microorganisms" (Lundström et al., 2000). These organic acids participate in weathering soil minerals, dissolving Fe and Al oxides and reducing ferric Fe compounds (Lundström et al., 2000). Al and Fe complex with humic and fulvic acids resulting in their mobilization and translocation. Al and Fe are precipitated or adsorbed, forming the Bs or Bhs horizon. The immobilization of Al and Fe may occur "when sufficient amounts of Al and Fe are adsorbed to form large immobile, polymerized organo-metallic compounds, or through desiccation, or when a horizon with different ionic concentration or acidity is encountered. Precipitation of sesquioxides may result from oxidation of the organic component of the complex" (Mokma and Buurman, 1982).

It is also suggested that microbial decomposition of the organic complexes cause deposition (Mokma and Buurman, 1982; Lundström et al., 1995). Organic acids are degraded by heterotrophic microorganisms as they move downward through the soil profile, indicated by increase in pH, temperature changes, changes in DOC and precipitation of Al (Lundström et al., 1995). Since changes in pH are apparent in a few years, they have been used as an indicator of changes in podzolization rates (Miles, 1985a).

Microorganisms in the soil degrade organic acids, resulting in the release of Al and Fe ions and their precipitation. Sterile and non-sterile soil columns displayed significant differences in the mobilization and immobilization of Al and Fe, suggesting the importance of microbes in degrading the organic ligand and promoting precipitation of Al and Fe (Lundström et al., 1995).

Plants

Canopy through fall, stem flow and leaf litter leachate are sources of low molecular weight organic acids (LMWOA) in soil. In addition, roots and microorganisms within the soil provide organic acids. Microbial activities can transform organic acids. The amount and type of organic acids vary with the plant type. There is a relationship between the plant species and organic compounds in a soil (Whitehead et al., 1982).

Acidifying plants are commonly associated with podzol development. These plants have been studied to better understand their allelopathic effects as well as soil effects (Mallik and Pellissier, 2000; Gallet and Keller, 1999; Gallet and Pellissier, 1997; Jaderlund et al., 1996; Gallet, 1994; Kuiters and Denneman, 1987). Leaf litter from white pine, spruce, heath and vaccinium (blueberry and bilberry) has been found to have high levels of polyphenols and phenolic compounds (Kuiters and Denneman, 1987). These compounds are beneficial in nutrient-poor environments by reducing the rate of nitrogen mineralization and slowing decomposition (Kuiters, 1990). This can increase nutrient availability for the plants during times of high demand, such as in spring. Phenolic compounds often inhibit the growth of other plants and microbial activity thereby reducing competition and decomposition rates. Ericacea and white pine litter have been found to decompose slowly (Cornelissen, 1996). The decreased rate of biological activity in these soils may account for higher levels of humic and fulvic acids (Nielsen, 1987). In acidic conditions these organic compounds tend to remain soluble and active and consequently available to complex with Al and Fe. Relatively high levels of monomeric phenols, including protocatechuic acid, vanillic acid and p-hydroxybenzoic acid were found in podzolic soils with pine, spruce and bilberry (Mallik and Pellissier, 2000; Kuiters and Denneman, 1987).

Aqueous leaf litter extract from podzolizing plant species varies through the year, as does the phenolic content of soils (Kuiters and Denneman, 1987). Studies suggest that the leaf color may be an important indicator of decomposition rate, green color indicating earlier, more rapid, stages of decomposition compared to brown colored leaves in later, slower decomposition stages (Cornelissen, 1996). Leachate from senescing bilberry leaves showed higher levels of phenolics than decomposing leaves, furthermore, rinsing the senescing leaves also lowered the level of phenolics in the leachate. This suggests "brown coloration represents mostly phenolic compounds such as lignins and tannins that become apparent in senesced leaves once the green pigments have been transformed into colorless compounds." Water-soluble phenols were found to leach readily from leaf litter

(Kuiters, 1990). This early loss of organic acids supports the lower pH values observed with extracts from greener leaf material from blueberry plants compared to higher pH values from browner leaves. The apparent increase in Al mobilization and aggregation is also supportive of the rapid leaching of phenolic compounds from leaf litter into the soil. Lundström (1993) found seasonal variations in Al and Fe as well as organic acids due to increased leaching in the autumn, also a lower soil pH. In top layers higher proportions of Al were complexed with organics. "Lower quantities of phenolic acids were generally found in the more decomposed litter," due to "degradation by microorganisms or abiotic and biotic catalytic polymerization and incorporation into water insoluble humic type substances" (Pohlman and McColl, 1988). The amount of phenolic compounds in soil is related to litter type and amount of carbon in soil. During humification of plant residue into soil organic matter there was a reduction in amount of phenolic compounds in soil (Whitehead et al., 1982).

Soluble plant polysaccharides and carbohydrates released from leaf litter decomposed rapidly to low molecular weight acids by the action of micro organisms (Pohlman and McColl, 1988). Chelating ability is related to the structure of the organic acid, oxalic, malic, gallic and protocatechuic acids have high chelating abilities (Pohlman and McColl, 1988). Organic compounds containing β-hydroxy functional groups, and phenolic acids contain ortho-hydroxyl groups were more effective chelators of Al than other similar compounds with other functional group combinations (Pohlman and McColl, 1988). Organic acids and polyphenolic compounds from plant litter and its decomposition were "principal agents causing Al and Fe dissolution in forest soils." Litter also buffers soil. Buffering effects of litter largely resulted from hydrolytic interactions with litter, and cation-exchange processes with humic and mineral components of soils resulting in solubilization of organic and metals (Pohlman and McColl, 1988). Differences in organo-metallic compounds were related to differences in the litter at the different sampling times.

Water-soluble organic acids have a direct effect of acidifying soil. Decreasing pH has the effect of solubilizing Al^{3+}. This increases the availability of Al for complexing reactions with organic acids. Organic acids can sorb onto soil particles, reducing exchange sites for ions to bind. Al formed stable complexes with organic acids such as protocatechuic acid because of its ortho hydroxyl sites (Vance et al., 1986). Al complexes were transported in the soil water. Microbial activity can polymerize the monomeric complex, increasing the size and resulting in insoluble forms that precipitate. This complex can act as a cementing agent in the B horizon. Over time, the carbon compounds decrease, leaving the lower B horizons with less C (Barrett and Schaetzl, 1998). This is reflected in color and C content of lower B horizons compared to younger, upper B horizons.

Organic acids

Organic acids present in soils vary according to plants and microbial action. Podzolizers (pine and spruce) had higher levels of ferulic acid and ρ-courmaric than depodzolizing species (oak, birch and beech) (Kuiters and Denneman, 1987). Phenolics in a spruce forest were found to stimulate some microbial communities while inhibiting others (Suoto et al., 2000). Soil microorganisms produce organic acids that may be important in complexing and transporting Al in the rhizosphere. It has been found that rhizosphere fungi release complexing organic acids (Devevre et al., 1996). The nature of organic acids produced by ericoid mycorrhizae is not known.

Organic acids are thought to play an important role in the translocation of sesquioxides in Spodosols. The reactivity of LMWOA was dependant on their noncomplexed concentration in the solution (Evans, 1998). In addition, "substantial microbial degradation of organic acids occurred within a relatively short time period" suggesting that high concentrations of LMWOA are more effective in the podzolization process, however these organic acids may have a brief residence time. Much lower quantities of phenolic acids were generally found in more decomposed surface litter due to degradation by microorganisms or abiotic and biotic catalytic polymerization and incorporation into water insoluble humic type substances (Pohlman and McColl, 1988).

In the formation of spodic horizons Al is precipitated with organic and inorganic compounds. Immobilization of Al can resulted from increases in pH, polymerization, desiccation and/or microbial decomposition of organic acids. Al-OH polymers are encouraged by organic matter such as fulvic acids (Simonsson, 2000). Stable soil aggregates and cemented horizons (i.e. ortstein) can be formed by the sorption of organic complexes into large particles through bridging of polyvalent cations (e.g., Al^{3+}, Fe^{3+}, Ca^{2+}) (Sposito, 1996). It has also been suggested "that high-molecular-mass complexes can act as cementing agents between clay particles" (Sposito, 1996; Goh and Huang, 1986). "Under proper pH conditions trivalent cations are effective in precipitating humic substances. Organic acids in the extract were able to bind particles to form surface aggregates" (Stevenson, 1982). This processes was enhanced by wet/dry cycles (Simonsson, 2000).

Type and level of organic acids in soil and roots varied with the plant type (Whitehead et al., 1982). As these organic compounds are decomposed there is a trend towards more uniformity in organic matter. Lower levels of phenolic compounds were present in soil than in roots. After release from plants, organic compounds can be transported, sorbed or transformed. Fern plants showed higher levels of some common LMWOA in soil than in root material, with high levels of unidentified organic compounds in roots. Bracken fern generally showed low levels of phenolic compounds (Whitehead et al., 1982).

Bracken fern is often found in association with ericaceae and other podzolizing plants (Jarvis and Duncan, 1976). Bracken fern are responsible for the redistribution of sesquioxides in soil profiles after replacing heather, thereby increasing Al and Fe in A horizons (Jarvis and Duncan, 1976). Bracken fern generally had low levels of phenolic compounds, high numbers of unidentified LMWOA and the limited amounts of identified LMWOA were unusually distributed (Whitehead et al., 1982). Fern had higher levels of some of the common LMWOA in soil than in root material, with high levels of unidentified organic compounds in the roots. Low malic acid contents were found in bracken fern (Pohlman and McColl, 1988). Low levels of ρ-hydrobenzoic acid and high levels of ferulic and ρ-coumaric acids were found in soil under bent grass (Whitehead et al., 1983).

Some phenolic organic acids have the ability to inhibit root development and effect microbial activities. This has the secondary effect of altering the recycling rate of nutrients in the soil. Some microbes were able to utilize the C in the phenols, thereby degrading the phenolic compounds (Suoto et al., 2000). Phenolic compounds were also found to inhibit some plant growth (Gallet and Pellissier, 1997).

The overall decrease in total B horizon sesquioxides after the change to depodzolizing species suggests that they are lost, being remobilized and relocated within 100 years of the change in vegetation. This suggests that translocation of Al and Fe involves organic C and organically bound Al and Fe. Depodzolization was first noticeable in the organic C and organically bound Al and Fe (Barrett and Schaetzl, 1998).

Al and Fe

Al and Fe are considered acidic ions because they are able to replace H^+, thereby contributing to the total acidity of soil. Al chemistry in soils is complex and pH dependant. Al speciation in soils depends on such factors as pH, content of dissolved organic acids, and types of competing inorganic ligands. Al can exist primarily as free Al^{3+} radicals below pH values of 4.7. In solution Al^{3+} is octahedrally coordinated to six water molecules (Huang and Violante, 1986). The organic acids present in soil also play an important and dynamic role in Al speciation (Sposito, 1996). Al commonly forms inorganic and organic complexes. Al can form compounds with silica, phosphorous and other anions. Al complexation with P at low pH is an important factor in the unavailability of P in acidic soils. Al can form a variety of amorphous compounds as well as silicate minerals. Al hydroxide speciation is pH dependent, as the pH increases hydrolysis reactions form Al(OH). Al can be taken up by soil organisms and sequestered by mycorrhizae (Yang and Goulart, 2000). Strongly complexed/occluded Al can be held in organic polymers that act as an Al sink. Al can also sorb onto clays and organic matter.

Al complexes with biochemical compounds from microbes and plants such as LMWOA, phenolics and polyphenolics as well as humic and fulvic acids.

Organic acids complex with polyvalent cations such as Al^{3+} by displacing H^{+} in functional groups, particularly $COOH^{-}$ and OH^{-}. Deprotonation and protonation of soil organic matter acts as a buffering mechanism in soil (Simonsson, 2000). Exchange of H^{+} to Al^{3+} may not result in the net charge exchange ratio of 3:1 being constant, variation in the exchange ratio may be a result of complex-binding with multiple functional groups (multidentate) and/or hydrolysis of organic bound Al (Simonsson, 2000).

Organic acids with two juxtaposed OH^{-} groups form very stable bonds with polyvalent cations. The two protons are released and the Al binds with both oxygen atoms, forming a very stable molecule. This arrangement is present in a number of organic acids, phenols and polyphenols, including protocatechuic acid. Protocatechuic acid has been related to the formation of spodic horizons in Michigan soils (Vance, 1984). Protocatechuic acid can be a degradation product of organic acids such as vanillic acid and p-hydroxybenzoic acid (Vance et al., 1986; Sposito, 1996).

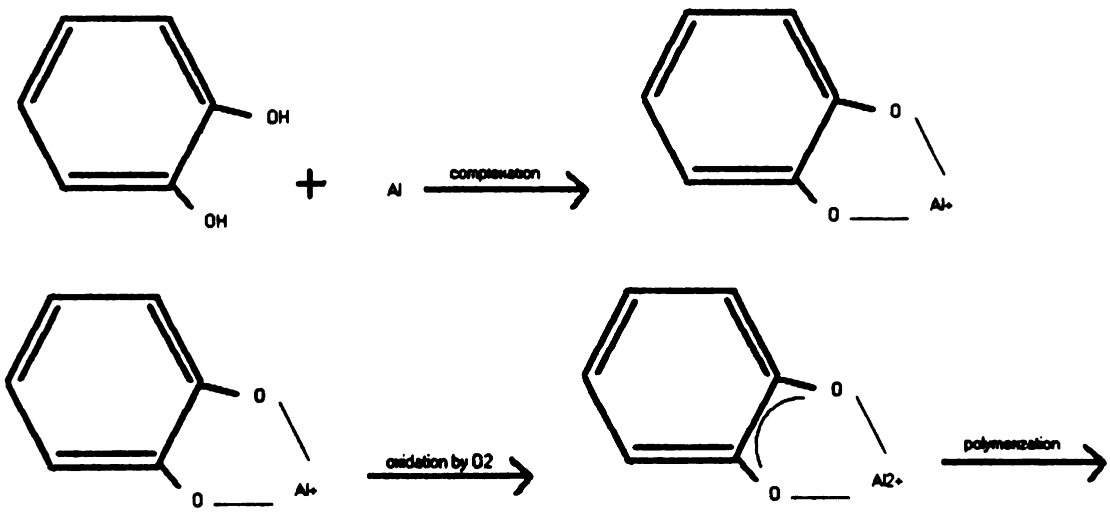
Organo-metallic complexes can remain soluble and move through soil. As they move and encounter additional Al^{3+} and complex with them leaching increases. Complexation with organic compounds controlled mobility of Al in upper horizons of Spodosols (Simonsson, 2000). At pH values between 5 and 7 chelating organics increased Al solubility (McBride, 1994). Al solubility increased with increased Al binding to organic matter. This continued until the organic matter was saturated, then Al solubility was controlled by inorganic properties such as hydrolysis reactions (Simonsson, 2000).

"The ability of low-molecular weight organic acids to release P and Al from soils is well established and has been related to the stability constant of the ligand" (Fox et al., 1990). Organic acids with larger $logK_{Al}$ values tend to release more Al than those with smaller $logK_{Al}$ values, although this is not consistent. $LogK_{Al}$ values are not available for all organic acids, however those that are available do indicate that higher $logK_{Al}$ values do correlate with higher chelation of Al.

Polymerization

Al complexes, both organic and inorganic, can exist as stable mononuclear molecules or can polymerize. Polymerization of Al-organic molecules occurs as molecules coalesce or additional molecules are joined onto the organo-metallic complex. Three mechanisms have been proposed for the polymerization of Al complexes; hydroxyl bridges, cation bridges and microbial oxidation. Similarly inorganic Al-complexes can also polymerize. These activities can occur through oxidative reactions that lower the net ionic charge of Al, neutralize the compounds and affect the acidity of the environment. Complexation of metal cations such as Al^{3+}, which acted as building units in the oxidation of polyphenols to polymeric quinines, increased the rate of polymerization (Stevenson, 1982). The ability of OH^- to donate an electron made these compounds susceptible to oxidative degradation. Biological decomposition of organic molecules can polymerize molecules and supply energy and C for organisms. Formation of polymers from monomorphic organic compounds also tends to increase the pH. Polymerization of organic complexes can increase the molecular weight, low molecular weight organic acids can polymerize and form high molecular weight compounds (humic acid) that can act as a sink for polyvalent cations (Stevenson, 1982). Degree of polymerization is controlled by many factors including pH and concentration and nature of cations and organic ligands.

Hydroxyls can act as bridges in the formation of inorganic polymers, this was strongly effected by pH (Huang and Violante, 1986). "When Al is added to a system containing humic materials, protons are released when Al^{3+} displaced H^{+} from binding sites in the humus and when hydrolyzed Al species or precipitates of $Al(OH)_3(s)$ were formed" (Simonsson, 2000). Hydrolysis of complex-bound Al, or multidentate complex-binding, or both, might be extensive. "Thermodynamics predicts chelation by the ortho-hydroxy Os to be more favorable than complexation by the carboxyl group due to a greater increase in entropy with the release of two protons in chelation" (Sikora and McBride, 1990).



(after McBride, 1994)

Gel

Soil-water solution remains trapped on particle surfaces during drying and accumulates at particle interfaces. DeConinck (1980) described, "the formation of large immobile "polymerized" organo-metallic compounds. Because these compounds contain much hydrophilic water, they form a gel. This gel-like substance was high in Al and organic matter (Lee et al., 1988a). "Transition into the solid state is accompanied by the loss of most of the hydration water. At a certain stage of the dehydration process Van der Vaals bonds and protonic bridges can form and bring about a certain degree of hydrophobicity." (DeConinck, 1980) The interstitial carbon-Al gel dries and forms a cement that holds particles together.

Gel-like substances were identified as contributing to the cementation of ortstein materials in Florida Spodosols (Lee et al., 1988a). The exact nature of the gel-like substances was not identified, but it was determined to be predominantly Al-organic matter complexes.

An increase in pH was observed in dried soils, and was "the result of an enhanced ability of soils to neutralize added or inherent acidity" (Simonsson, 2000). Increased Al solubility after drying may be due to mineral dissolution resulting from drying. Organic matter was altered by drying. The organic structure developed ruptures due to desiccation and "drying led to increased solubility of Al and enhanced neutralization of H^{+}" (Simonsson, 2000). Microsites at aggregate surfaces may increase in pH during wet/dry cycles.

Immobilization of Al in soils can occur as a result of cationic bridges, proton and polyvalent cations (DeConinck, 1980). This would remove cations and protons from solution and increase the pH. Polyvalent cations are important in binding soil particles. Binding of organic anions by clay is possible when a polyvalent cation is present on the exchange complex. The cation neutralizes the charge on the surface as well as the acidic groups of the organic molecule to form salt bridges. The pKa of humic substances is influenced by the amount of ionic salt. At pH of the soil below the pKa of the organic substance, some sorption was possible (Stevenson, 1982). Metal ions form bridges between organic matter and soil constituents.

Hydrophobic molecules

Soil particles in surface layers occasionally display hydrophobic tendencies, repelling water. The dehydration process has been related to the development of hydrophobic molecules (Stevenson, 1982; DeConinck, 1980). It has been postulated that hydrophilic humus molecules change to hydrophobic-types of colloids when an electrolyte is added to a solution. In solution hydrophilic polymers are extended due to mutual repulsion of acidic units within the macromolecule. When cations are present, the acidic functional groups are attracted to the cations, thereby reducing internal repulsive forces. This is particularly apparent with polyvalent cations such as Al^{3+} and Fe^{3+}. The reduction in internal repulsion "favors coiling of the (polymer) chain and causes a reduction in the amount of hydration water held by the colloid." (Stevenson, 1982) This is consistent with higher concentrations of C in the surface, aggregated materials, suggesting that the cementing agent is carbon. At a certain stage of the dehydration process Van der Vaals bonds and protonic bridges can form and bring about a certain degree of hydrophobicity" (DeConinck, 1980).

The formation of cemented spodic materials has been described as a snowball effect (DeConinck, 1980). " The progressive cementation begins to impede the penetration and development of roots. Accelerated cementation progressively decreases root and biological activity and subsequent fossilization of the horizon." This snowball effect may also be involved in the removal of Al^{3+} from the available ion pool. This decreases the total acidity, increasing pH, and reducing the solubility of Al^{3+}. In addition biological degradation of Al-organo-metallic complexes supplies C and energy to microbes, tending to increase the microbial population and increase the potential for biodegradation of these complexes.

As soluble organo-metallic complexes moved through soil and encountered additional Al, they were able to complex some Al, increasing the Al:C ratio. This increased concentration of Al in lower layers contributed to immobilization. Increased ionic strength caused more bonding with cations and an increase in size of the molecule. As the complexes increased in size, they became less soluble. Both the size and configuration of the polymers along with pH changes contributed to decreased solubility. Complexed Al by deprotonated carboxyl groups changed the expanded structure of the Al-complex to a condensed configuration, reducing the solubility (Sposito, 1996). "As chain-like structures are formed, and as oxygen-containing functional groups become neutralized, precipitation increased." With these increases in pH due to oxidative reactions in coupling molecules to form polymers and reducing the net change of the Al ion, Al solubility decreased. Inorganic Al hydroxide polymers formed as well as organic polymers. As the Al:OH ratio increased, so did the formation of Al(OH) polymers (Huang and Violante, 1986).

Root Pressure

Plant roots exert pressure as they grow through soil. The ability of roots to pass through materials is related to soil penetrability and root-growth-pressure exerted by the plant. The ability of roots to exert force and penetrate soils is related to plant species. Maximum axial root growth pressures were similar for dictyledons (0.41 MPa) and monocotyledons (0.44 MPa) (Clark et al., 1999a). Maximum axial growth pressure of pea seedling (*Pisum sativum L.*) roots ranged from 0.3 MPa to 1.3" (Clark et al., 1999b). Roots tend to thicken and cellular turgor pressure increases under mechanical stress. Roots with larger relative root diameters tend have a greater ability to penetrate soils (Materechera et al., 1992). The positive correlation between root pressure and diameter suggests that the size of a root has a significant influence on its ability to penetrate strong soil layers. "This could be related to the effects which root diameter may have on root growth pressure and on the mode of soil deformation during penetration." Under mechanical pressure from soils with low penetrability roots tended to increase in thickness and decrease elongation rates.

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CHAPTER 2

Rate of Recementation of Crushed Ortstein

Abstract:

Blueberries in isolated regions of blueberry fields in Michigan experience reduced growth. Growers have attempted deep tillage to breakup ortstein in these regions with only temporary benefits. This study was conducted to determine if: a) crushed ortstein would recement, b) the rate of recementation of disturbed ortstein, c) the degree and strength of cementing and d) the nature of the cementing agents. Crushed ortstein from Saugatuck sand (Typic Durorthod, sandy, mixed, mesic) was passed through a 2 mm sieve and used in column experiments to assess recementing. Aqueous blueberry leaf extracts were added to crushed ortstein columns for 1½, 3, 6, and 12 week periods. Green blueberry leaves and brown leaves were used to prepare extracts and compare the effect of leaf age on aggregation. The degree and strength of aggregation were assessed by determining the amount of treated ortstein remaining on a 2 mm sieve and by tensile strength analysis of aggregated material. Ammonium oxalate extracts and direct coupled plasma were used to assess Al and Fe distribution. OM was determined by loss-on-ignition method. Changes in color and pH were assessed. Recementation of crushed ortstein began within 1½ weeks. Cementation and pH were highest in the upper layers and decreased with depth in the column. Al was relocated vertically and horizontally in the column. OM appear to have been the cementing agent in the upper layers and Al-containing compounds in the lower layers. Aggregated materials had higher Al and lower OM in the lower layers. Degree and strength of cementation tended to increase with

duration of the experiment. Green leaves were more effective than brown leaves in recementing crushed ortstein.

INTRODUCTION

Blueberry growers in southwest Michigan have experienced diminished growth in some blueberry replants. This occurs in isolated regions of fields, in which the remainder of the replants have reached full size and production. In Michigan, blueberries (*Vaccinium corymbosum* L.) are grown primarily on Spodosols, some of which have ortstein layers. Ortstein, also known as hardpan, varies in occurrence and thickness within the fields. Ortstein has been known to reduce blueberry growth (Lilly et al., 1975). It has been suggested that the ortstein layer acts as a barrier to water and root penetration. Growers have attempted to break up the ortstein layer with deep tillage prior to replanting blueberries. This has not been a permanent solution. Some growers believe that the ortstein has reformed (Vern Brower, 1999, personal communication).

The objectives of this study were to determine: 1) if crushed ortstein would recement, 2) speed of recementation, 3) degree and strength of recemented materials, and 4) the nature of the cementing agents.

MATERIALS AND METHODS

Ortstein samples were collected from a blueberry field near West Olive, MI. A trench was dug in Saugatuck sand (Typic Durorthod, sandy, mixed, mesic) which has a well-developed Bhsm (ortstein) horizon at about 8-20 inches, generally >10 inches thick (Mokma et al., 2000). Cemented Bhsm horizon material was extracted from the sidewalls. The material was then air dried, crushed and passed through a 2.0 mm sieve.

Blueberry leaves were collected from blueberry plants as well as under the plants, cleaned and stored in a cooler at 5°C. Extract solutions were prepared fresh weekly by placing crushed leaves in distilled water (1g:10 ml ratio). This mixture set for 24 hours at 20°C. The extracts were more concentrated than natural solutions, this would tend to speed up results. The extract was filtered using a Buchner funnel and stored at 5°C.

Cylindrical, plexiglass tubes 30 cm in length and 11.5 cm inside diameter with temperature ports at 5 cm, 15 cm and 25 cm depths, were mounted vertically. The bottom was held with cheesecloth. Crushed ortstein material was placed in the columns. While adding crushed ortstein to columns there was some segregating of particles and layering within the columns, mixing and sequential addition of material to columns reduced this effect. Three replicates per treatment were established and run for 1½, 3, 6, and 12 weeks and maintained at room temperature. Water was used as a control. Crushed leaf material was placed on the surface to protect the surface, distribute extract and reduce evaporation. Slow decomposing, pine wood mulch was used on the surface of the control, water treated columns. Water or blueberry extract (20ml) were applied daily in a one minute interval spread over the surface area, this is approximately twice the rate of precipitation in the region.

The effect of the age and quality of leaves was assessed using fresh, green leaves, collected early in the season (June 2001) and comparing these to brown, decomposing leaves that were collected at the end of the season (November 2000). The fresh leaves were removed from blueberry plants, dried and stored at 5°C. Extract was prepared daily for fresh, green leaves and weekly for decomposing leaves. The ability to store leaf extract was evaluated by assessing extract of various ages, stored at 5°C, using High-pressure liquid chromatography (HPLC).

HPLC was used to identify and compare low molecular weight organic acids (LMWOA) present in the extract. HPLC analysis was achieved using absorbance detection at 280 nm, 1.0 ml/ min. flow rate and 5% acetonitrile, 95% acetic acid (1%) elution (Vance et al., 1985).

Temperature data were collected from the columns at 5 cm, 10 cm and 15 cm depths at the end of treatments. Completed columns were allowed to air dry and then separated in 3 cm increments. The materials were sieved through a 2.0 mm sieve. The percentage of aggregated material that remained on the sieve was determined.

Aggregates were assessed for their structural tensile strength by the aggregate crushing technique (Dexter and Kroesbergen, 1985). Ortstein pieces were placed in a mist chamber (nebulizer) for 24 hours, set in plastic bags for 24 hours and then gently broken up along natural aggregate breaks and allowed to air dry. The samples were sieved through 6.3 and 9.5 mm sieves. Representative aggregates were selected for tensile strength analysis.

Aggregates were placed on a balance and the crusher initiated. The maximum force required to deform or break an aggregate was recorded. For aggregates that gradually deformed the maximum stress required to initiate the deformation was recorded. For aggregates that break abruptly, the appropriate peak strength was recorded. The crushed aggregate was weighed, placed in an oven for 24 hours and then weighed again. The air-dried and oven-dried weights were used to calculate percent moisture of the air-dried aggregates for tensile strength determination (Dexter and Kroesbergen, 1985; Smucker, 2001, personal comunication).

Al and Fe concentrations were determined for loose and aggregated soil samples, at 3 cm depth increments, using ammonium oxalate extraction (Soil Survey Staff, 1984) with 200ml of solution and 2 g of soil shaken for 4 hours in darkness, then direct current plasma emission spectroscopy (DCP) analysis. DCP was rinsed regularly with dilute nitric acid to clean the DCP column. Organic matter was determined by the loss-on-ignition method (Schulte, 1988), and pH was measured using 1:1 soil-water mixture (Soil Survey Staff, 1984).

Additional columns were set up to evaluate the effects of leaf quality using brown, decomposing blueberry leaf extract. Treatments were run for 1½, 3 and 6 weeks.

Data from this study were analyzed using Mixed model procedure (Proc mixed) with repeated statement in SAS statistical software. The logarithmic transformation was applied to weight and strength data to provide normality assumption for analysis. Differences between treatments were determined by using least squared means (LSMEANS) differences in the ($p<0.05$) significance level with the Tukey-Kramer adjustment.

RESULTS AND DISCUSSION

The green (fresh) blueberry leaf extract was light, yellow-brown colored while the brown (decomposing) leaf extract was dark and opaque. The green blueberry leaf extract had lower pH (pH=3.5) compared to the brown leaf extract (pH=4.5). Green leaf extract contained more simple, low molecular weight organic acids, most likely including protocatechuic acid, vanillic acid, ρ-hydroxybenzoic acid and possibly catechol than brown leaf extract, possibly as a result of the formation of polymers and precipitates.

During the treatments some columns had extract ponded on the surface and limited amount of leachate passing through the column, this primarily occurred in the columns treated with fresh blueberry leaf extract where the average leachate was 10 ml/day while 16 ml remained ponded on the surface at the end of the treatment. This suggests that permeability had decreased. A fermenting odor was present in these circumstances, suggesting anaerobic conditions existed within the column.

In several columns fruit flies were present at various life stages (eggs, larvae, pupae and adults were in the columns). A few columns had fungal mats visible between the litter layer and the crushed ortstein. Anaerobic conditions led to a fermenting odor. These observations were not related to length of treatment.

After extract or water had been added for the prescribed period, the columns were opened and the soil was allowed to air dry. The top and sides of the crushed ortstein (2.5 YR 2.5/3) treated with brown, decomposing leaf blueberry extract had dark staining (2.5 YR 2.5/1 and 2.5 YR 2.5/2). Those treated with fresh blueberry leaf extract also had dark coatings (7.5YR 3/2 to 7.5YR 2.5/2). Dark coatings were also present on some aggregated materials in lower layers, particularly those adjacent to column walls. Decreased values indicate an accumulation of OM, Al and Fe. The extent of the dark coatings increased with duration of treatment.

The columns showed high levels of cohesiveness at the top, decreasing downward, in general this increased with the duration of the treatment. The sides and top tended to have more cohesion than the center. Columns treated with fresh blueberry leaf extract were more cohesive than those treated with brown, decomposing leaf blueberry extract.

Aggregation

Aggregation in columns treated with blueberry leaf extract was much greater than those treated with water. The amount of ortstein material that remained on the 2.0 mm sieve was greater with green leaf extract than with brown leaf extract (Figure 1). The top layers of the columns were highly aggregated. Fresh, green blueberry leaf extract treatments had greater aggregation in the top layers (0-3 cm) and at depth than the brown blueberry leaf extract treatments. Aggregation increased with treatment duration, indicating that aggregation and cementing increased with time. Cementation increased with depth over time as well (Figure 2). The amount of aggregation in the top 3 cm was not significantly different in the 1½, 3 and 6 week green blueberry leaf extract treatments, although aggregation tended to increase with duration of treatment at depth.

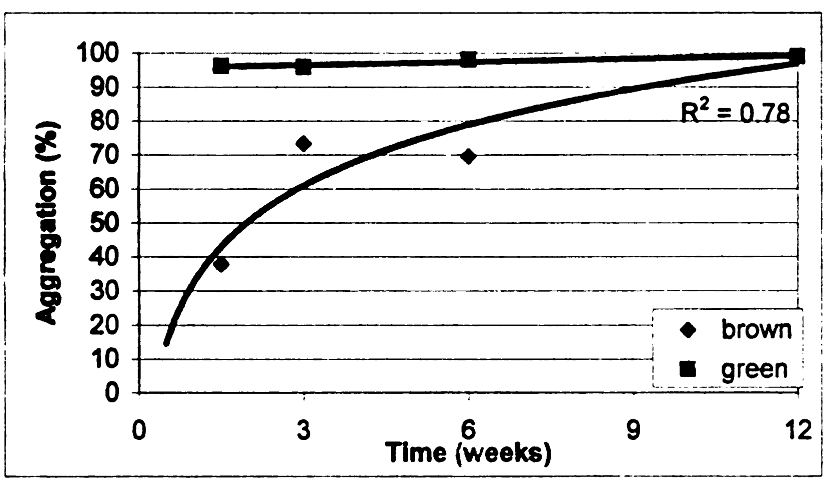

Figure 1. Aggregation in top layer (0-3 cm) for green leaf extract and brown, decomposing leaf extract.

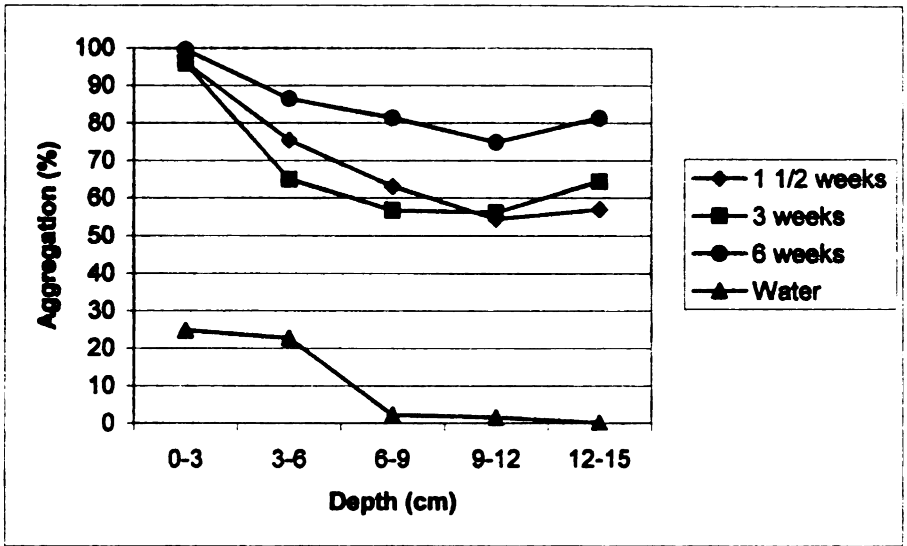

Figure 2. Aggregation (percent remaining on 2mm sieve) with depth in column and duration of green blueberry leaf extract addition.

The 1½-week green blueberry extract columns exhibited significantly ($p<0.05$) higher percentage of aggregation than the 1½-week brown blueberry leaf extract columns (Figure 3). The 1½-week brown blueberry leaf extract treatment had significantly less aggregation than the longer treatments, the difference and significance increasing with depth and duration.

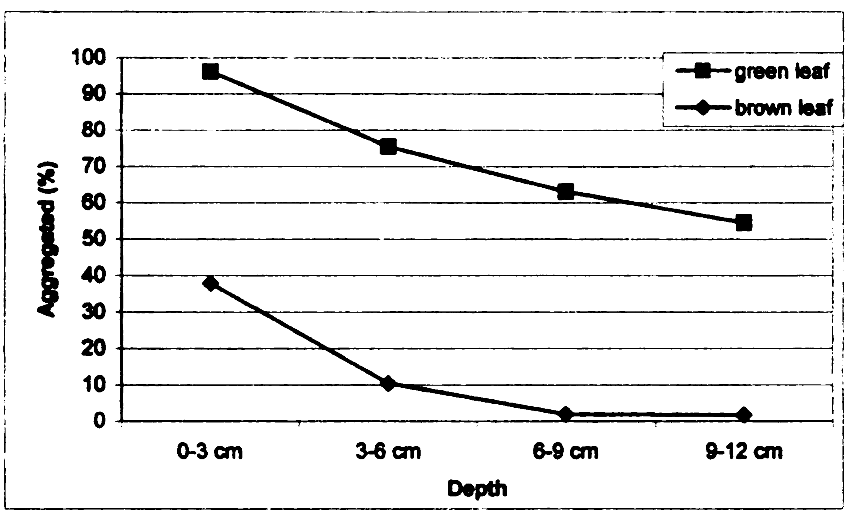

Figure 3. Aggregation after 1½ weeks for green and brown blueberry leaf extract treatment.

Tensile Strength of Aggregates

In general aggregate strength increased with duration of treatment (Figure 4). Tensile strength of the aggregates that received green leaf extract was greater than that of those that received brown leaf extract (Figure 5). Upper layers displayed more strength than lower layers. Root pressure has been recorded at less than 1 MPa (Clark et al., 1999), this is exceeded by some materials after the 1½ weeks treatment. Over 95% of the top layer aggregates (0-3 cm) and 50% at the second layer (3-6 cm) exceeded 1 MPa after 1½ weeks treatment with green blueberry leaf extract. While this does not indicate that aggregated materials cannot be penetrated by roots, it suggests that the cemented materials may effect root growth.

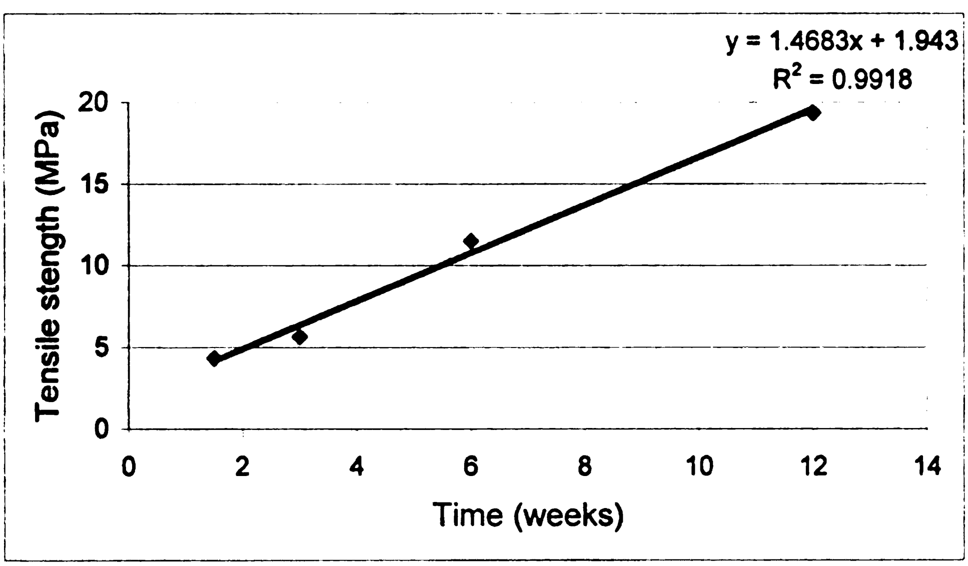

Figure 4. Tensile strength of aggregated material in top layer (0-3 cm) with time of green blueberry leaf extract addition.

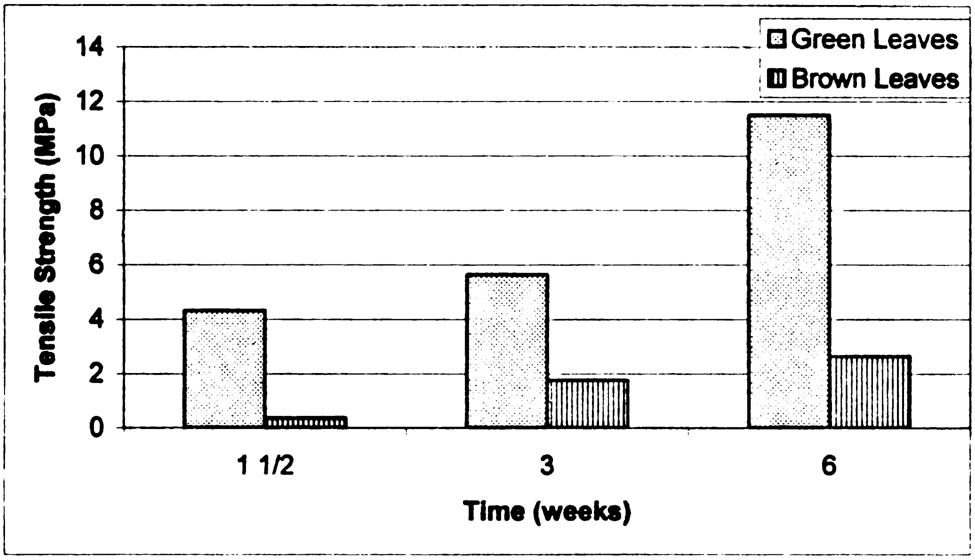

Figure 5. Aggregate tensile strength for green and brown leaf extracts over specified duration for surface layer (0-3cm).

Cementing agents

Aggregates in upper layers had more OM and less Al than in lower layers. Aggregates in the upper layer had more OM than loose materials; at depth there was less difference between loose and aggregate materials (Figure 6). Al was generally higher in aggregated materials than in loose (Figure 7), top layers had less Al than lower layers. The lower OM concentrations at depth in the column suggests that some OM was immobilized at the surface and played a role in the aggregation process there. In lower layers aggregates had less OM, however, Al was higher in aggregates than in loose material suggesting Al or Al-containing compounds are the primary cementing agent. The increase in Al with depth suggests eluvial processes transported some of the Al downward. Iron concentrations were low, less than 2 mg kg^{-1}, throughout the column suggest that Fe-containing compounds are not important in aggregating the crushed ortstein materials.

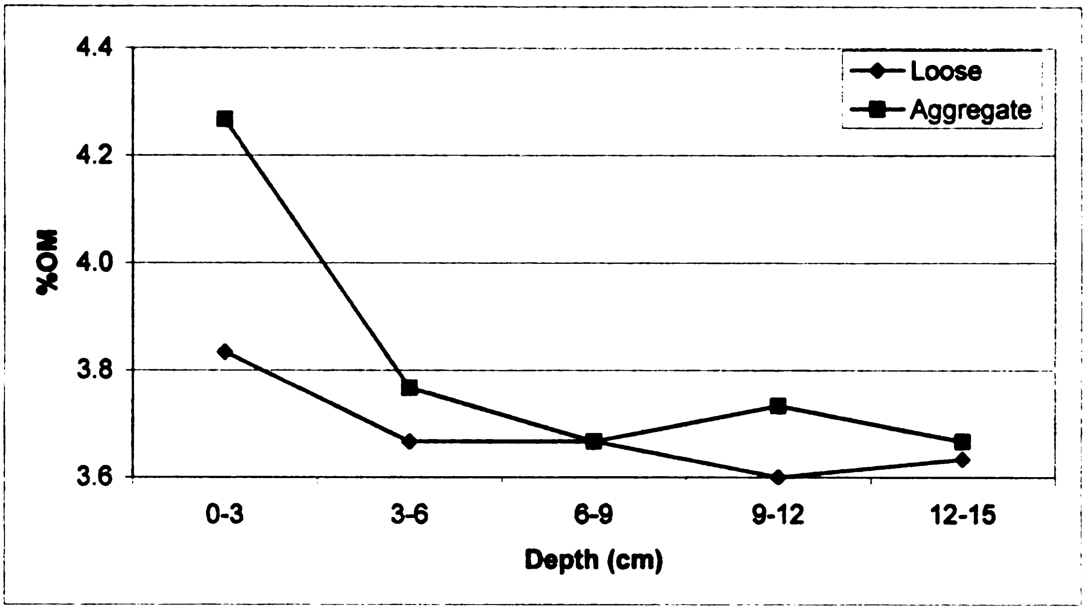

Figure 6. Distribution of OM with depth for loose and aggregate material with 3-week green blueberry extract treatment.

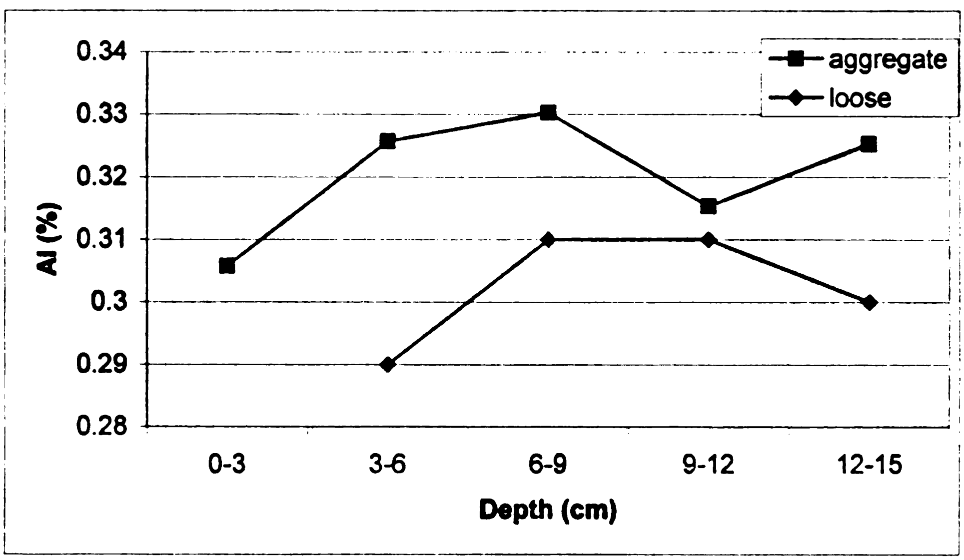

Figure 7. Al distribution with depth for loose and aggregate material with 6-week fresh, green blueberry leaf extract treatment.

Dark coatings were present on some aggregated materials in lower layers, particularly those adjacent to column walls suggesting preferential flow along the column sides. These aggregates had high C (4.78%) and high tensile strength, 2 standard errors above the mean.

Al and pH in loose material were negatively correlated. This is consistent with the mobilization of Al at lower pH. The relocation of Al within the layers of the column as well as downward through the column suggests that several processes are operating simultaneously, relocating Al both vertically and horizontally within the columns.

pH

The original ortstein had a pH of 4.5. pH of the green blueberry leaf extract was 3.5 and that of the brown blueberry leaf extract was 4.5. Initially the pH increased in the upper layers of columns, but later it increased in deeper levels with both green and brown blueberry leaf extract treatments. Aggregated portions of the soil had a greater increase in pH than loose soil although at depth that difference ended, this may be related to the depth of extract penetration in the columns (Figure 8). The pH of the surface layer of crushed ortstein increased as length of treatment increased. The increased pH suggests that the organic acids have been decomposed by microbial action within the soil column (Lundström, 1995). This was supported by higher temperatures in the columns receiving blueberry extract than those receiving water. The increase in pH and aggregation at depth is consistent with microbial decomposition and polymerization of organic acids, which then acted as cementing agents in surface aggregates. The decrease in OM in aggregates with depth is consistent with microbial activities that utilize the OM resulting in neutralized, polymerized compounds of higher pH, lower OM and bound Al. OM, Al, and pH are interrelated in these materials. These interrelationships support the hypotheses that organics control the concentration of solution Al (Ross and Bartlett, 1996).

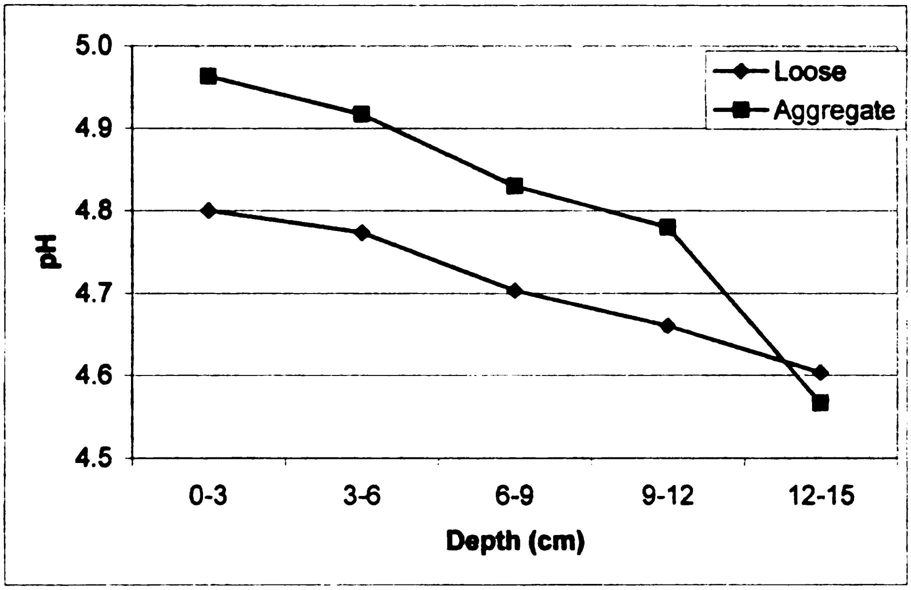

Figure 8. pH for loose and aggregate material of soil layers in columns with 3-week green blueberry extract treatment.

Many of the surface aggregate samples repelled water, suggesting some degree of hydrophobicity. This reduces solubility and water permeability of the OM, increases pH and sequesters Al. Functional groups in organic compounds are attracted to polyvalent cations such as Al^{3+}, causing a reduction in internal repulsion and resulting in coiling of organic polymers (Stevenson, 1982). This results in reducing the water of hydration held by the molecules and a "sink" for Al^{3+}. The Al^{3+} is less available for translocation.

In the initial crushing of the ortstein, cementing materials were fractured, exposing Al ions. With the addition of acidic blueberry leaf extracts these ions were readily solubilized. Water-soluble phenols were found to leach readily from leaf litter (Kuiters, 1990). This rapid loss of organic acids supports the lower pH values observed with extracts from greener leaf material from blueberry plants compared to higher pH values from browner leaves. The apparent increase in Al mobilization and aggregation is also supportive of the rapid leaching of phenolic compounds from leaf litter into soil.

In natural systems wet/dry cycles would occur frequently, increasing the degree of aggregation and podzolization. The experimental columns were wet throughout the experiment.

Blueberry fields are more dynamic and complex than the laboratory column experiments. After deep tillage, ortstein in blueberry fields is less broken up than in these controlled experiments. This would focus the flow of soil water solutions containing LMWOA and organo-metallic complexes in preferential flow patterns, increasing the rate of recementation. The effects of preferential flow were observed along walls in columns where increased aggregation and aggregate strength was evident. The irregular pattern of precipitation would also dilute soil water solution during high precipitation period and standing water would allow microbial decomposition of acids early in the cycle. Irrigation water with varying pH alters the natural system. Sequestration of Al in plant and microbial matter and soil buffering ability may also decrease Al transport within the soil profile.

CONCLUSIONS

The reaggregation of crushed ortstein began within 1½ weeks. Aggregation and aggregate strength tended to increase over time. Green blueberry leaf extract tended to increase the rate of aggregation and tensile strength of aggregates. This was apparent at the surface and with depth over time. The tensile strength of some aggregated material exceeded the force some roots have been known to exert. Percent of aggregated material was related to pH and Al, particularly with depth. Aggregated material had higher pH and Al contents than loose material from the same layer.

Aggregated materials at the surface had more OM and less Al, while those deeper in the column have less OM and more Al. This suggests that both OM and Al-containing compounds are responsible for the aggregation; OM serves as the primary cementing agent in the surface layers while Al-containing compounds act as the primary cementing agent with depth. Darker color, high OM, high tensile strength and higher pH are consistent with OM compounds as a cementing agent in the upper materials. Organic acids may have polymerized and become less soluble in lower layers. Organic polymers act as cementing agents and sinks for Al. Green leaves have more LMWOA, higher OM and lower pH, and are more effective at translocating Al and encouraging recementation of crushed ortstein than darker leaves with more organic polymers.

Blueberry extract can rapidly promote aggregation in crushed ortstein. Fresh blueberry leaf extract had high levels of low molecular weight organic acids (LMWOA). High concentrations of LMWOA, specifically organic acids which are better able to bond with Al such as protocatechuic acid (PCA), ρ-hydroxybenzoic acid (ρHBA) and vanillic acid (VA), tend to increase the rate of aggregation and translocation of Al.

The strong podzolizing effect of blueberries is most significant with fresh, green blueberry leaf extract. This suggests that in natural conditions rainfall on green blueberry leaves may dissolve organic compounds and carry them into the soil where they act as complexing agent, translocating Al and contributing to the formation of ortstein.

Aggregating processes in columns may differ from those in a natural setting. This experiment does suggest that several processes are involved in cementation, they occur both vertically and horizontally in the soil profile, and the involvement of organic acids derived from leaves. While the leaf extracts used in this experiment were more concentrated than those in nature and may have experience different decomposition processes and rates than naturally occurring, the experiments reflect the complicated nature of podzolization.

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CHAPTER 3

The Influence of Vegetation on the Reformation/Degradation of Disturbed Ortstein

Abstract:

Ortstein formation may cause decreased growth in blueberry fields in Michigan. This study was conducted to determine: a) the effect of podzolizing species such as blueberry and white pine and depodzolizing species such as bracken fern, bent grass and fescue in the recementation of crushed ortstein, the degree and strength of recemented material, the ability of depodzolizing species to reduce recementation, b) the effect of leaf extracts on the size and strength of ortstein pieces in crushed ortstein columns, and c) the effect of degree of leaf decomposition, rhizosphere and topsoil material on recementation of crushed ortstein. Crushed ortstein from Saugatuck sand (Typic Durorthod, sandy, mixed, mesic) was passed through a 2 mm sieve and used in column experiments to assess recementing. Aqueous leaf extracts were added to crushed ortstein columns for 12-week periods. The degree and strength of aggregation were assessed by determining the amount of treated ortstein remaining on a 2 mm sieve and tensile strength analysis of aggregated material. Ammonium oxalate extracts were used to assess Al and Fe distribution in the ortstein columns. Organic matter (OM) was determined by loss-on-ignition. Changes in color, temperature and pH were assessed. Podzolizer leaf extract had lower pHs and podzolizer treated crushed ortstein had more OM, greater aggregation, stronger aggregates and increased translocation of Al, lower pH and higher temperatures than depodzolizing treatments. Aggregates had higher Al, OM and pH than loose materials. Ortstein pieces treated with leaf extract from depodzolizing species tended to have decreased weight and/or strength. Green leaf extract was a more effective

podzolizer than brown leaf extract. Ap horizon material did not have a significant affect on recementation, however the rhizosphere did tend to decrease the translocation of Al and aggregation. Depodzolizing species may offset ortstein formation associated with blueberries.

INTRODUCTION

Blueberry growers in southwest Michigan have experienced diminished growth in some blueberry replants. While most blueberry replants have reached full size and productivity, plants in some isolated areas have reduced development, possibly due to ortstein forming an impenetrable layer. Ortstein has been known to reduce blueberry growth and development (Lilly et al., 1975). Blueberry growers have attempted to break up the ortstein layer with deep tillage prior to replanting. This has not been a permanent solution. Growers believe that disturbed ortstein has recemented (Vern Brower, 1999, personal communication). Recementation of crushed ortstein treated with blueberry leaf extract begins within 1½ weeks (Chapter 2).

The podzolization process and recementation requires the mobilization, translocation and immobilization of organic matter and sesquioxides. Organic acids present in blueberry leaf extract are able to complex with Al and Fe and transport them in the soil profile. Microbial degradation of organic ligands in the organo-metallic compounds result in the release and precipitation of Al (Lundstrom et al., 1995). Topsoil, Ap horizon, and rhizosphere materials contain large amounts of organic matter and micro organisms that may result in more rapid breakdown of organo-metallic compounds and the subsequent immobilization of Al.

Vegetation has been determined to induce podzolization and depodzolization (Dimbleby and Gill, 1955; Mokma and Buurman, 1982; Nornberg et al., 1993; Willis et al., 1997; van Breemen et al., 2000). Changes in vegetation have been found to reverse podzolization (Nornberg et al., 1993;Nielsen, et al., 1999; Barrett and Schaetzl, 1998).

In natural systems plants occur in association with many other species. These companion plants may ameliorate the podzolizing effects of blueberries (Chapter 2). Species such as oak, bracken fern, bent grass and fescue that naturally occur with ericaceae and have been reported in the podzolizing/depodzolizing cycle (Miles, 1978) may help maintain a dynamic equilibrium in the podzolization process in blueberry fields. In natural systems bracken fern is often associated with wild blueberries and white pine. In commercial blueberry production, a monoculture, the presence of depodzolizing, companion plants may help ameliorate the podzolization process.

White pine, a known podzolizer was used as a comparison for blueberry with water as a control. Suspected depodzolizing species such as bracken fern, bent grass and fescue were evaluated for their effect on the podzolization process.

The effectiveness of podzolizing species, blueberry and white pine, and depodzolizing species, bracken fern, bent grass and fescue, were studied for their ability to recement crushed ortstein or reduce the size and strength of pieces of ortstein. The potential of using depodzolizing plants in commercial blueberry fields to reduce progressive podzolization and recementation of disturbed ortstein was evaluated along with the effect of topsoil and rhizosphere on the process.

The objectives of these studies were to assess: 1) the effect of different vegetation in the recementation of ortstein, 2) the degree and strength of recemented material of crushed ortstein, 3) the effect of green blueberry leaves compared to brown blueberry leaves, 4) the ability of depodzolizing species to reduce recementation of crushed ortstein, 5) the effect of leaf extracts on the size and strength of ortstein pieces in crushed ortstein, 6) the effect of topsoil material on recementation of crushed ortstein, and 7) the effect of rhizosphere on recementation of crushed ortstein.

MATERIALS AND METHODS

Ortstein samples were collected from the study area (Saugatuck sand, Typic Durorthod, sandy, mixed, mesic) in a blueberry field near West Olive, MI. A trench was dug and cemented Bhsm horizon material extracted from the sidewalls. The material was then air dried, crushed and passed through a 2.0 mm sieve, pieces of ortstein were set aside for some column studies. This material was analyzed for pH, organic matter (OM), Al and Fe to establish the baseline of the crushed ortstein in the columns for comparison after treatments.

The role of vegetation in the reformation of ortstein was evaluated by adding extract from mixed (green and brown) blueberry leaves (*Vaccinium corymbus*), white pine needles (*Pinu strobus*), fescue (*Festuca*), bracken fern (*Pteridium aquilinum*), bent grass (*Agrostis*) and distilled water to columns containing crushed ortstein and ortstein chunks. Cylindrical, plexiglas tubes 30 and 10 cm in length and 11.5 cm inner diameter were mounted vertically. The bottom was covered with cheesecloth. Crushed ortstein material was placed in the columns. While adding crushed ortstein to columns there was some segregating of particles and layering within the columns, mixing and sequential addition of material to columns reduced this effect. Three replicates for all treatments were established and run for 12 weeks.

In another set of columns 5 weighed pieces of uncrushed ortstein were placed at identified locations beginning at 2cm depth with approximately 2 cm between pieces and horizontally offset, to be removed and evaluated for size and strength changes at the conclusion of the experiment. Each treatment was established using extracts of suggested depodzolizing species; bracken fern, bent grass, and fescue, along with white pine, a known podzolizer. Distilled water was used as a control. Crushed litter material was placed on the surface to protect the surface material, distribute extract and reduce evaporation. Slow decomposing, white pine mulch was used on the surface of the water control columns.

Blueberry leaves were collected from blueberry plants (green) and under blueberry plants (brown), cleaned and stored at 5 °C. White pine needles, fescue, bracken fern and bent grass leaves were collected and stored similarly. Extracts were prepared fresh weekly by placing crushed leaves in distilled water at a 1g:10ml ratio. This mixture was allowed to set for 24 hours at 20°C. The extracts were filtered using a Buchner funnel and stored at 5°C. Extracts were analyzed for pH and for organic acids by high-pressure liquid chromatography (HPCL).

The effect of topsoil was assessed using Ap horizon material collected at the study site. A 2-cm layer of Ap material was placed on columns containing crushed ortstein and treated with mixed blueberry leaf extract, fescue extract, bent grass extract, or bracken fern extract. Plugs of fescue and bent grass along with the Ap horizon and rhizosphere were added to additional columns. All columns were treated for 12 weeks with blueberry extract, bent grass extract or fescue extract. The grass was maintained with 10 hours of grow light exposure daily.

Water, blueberry, white pine, bracken fern, bent grass or fescue extract was applied daily at a rate of 20 ml, which is approximately twice the rate of precipitation in the region. The extract and leachate were tested for pH. HPLC was used to identify low molecular weight organic acids (LMWOA) present in the aqueous leaf extracts. HPLC analysis was achieved using absorbance detection at 280 nm, 1.0 ml/ min. flow rate and 5% acetonitrile, 95% acetic acid (1%) elution. (Vance et al., 1985)

Temperature data were collected from columns at 5 cm, 15 cm and 25 cm depths at the completion of the treatments. Completed columns were opened and allowed to air dry. Columns were separated into 3 cm increments. Samples were sieved and aggregation evaluated. The percentage of aggregated materials that remained on a 2.0 mm sieve was compared to the amount of loose material that passed through the sieve. Aggregates were assessed for their size and structural tensile strength by the aggregate crushing technique (Dexter and Kroesbergen, 1985).

Al and Fe concentrations were determined for loose and aggregated soil samples at 3 cm depth increments, using ammonium oxalate extraction (Soil Survey Staff, 1984) with 200ml of solution and 2 g of soil shaken for 4 hours in darkness, and direct current plasma emission spectroscopy (DCP) analysis. DCP was rinsed regularly with dilute nitric acid. pH was measured using 1:1 soil-water mixture. OM was determined by loss-on-ignition (Schulte, 1988).

Data from this study were analyzed using the Mixed model procedure (Proc mixed) with repeated statement in SAS statistical software. The logarithmic transformation was applied to weight and strength data to provide normality assumption for analysis. Differences between treatments were determined by using least squared means (LSMEANS) differences in the ($p<0.05$) significance level with the Tukey-Kramer adjustment.

RESULTS AND DISCUSSION

Ortstein in the columns generally exhibited more cohesion at the surface, bottom and near the walls. The blueberry and white pine columns were visibly more cohesive than those treated with fescue, bent grass and bracken fern, which began to fall apart while drying. Water treated columns showed very little or no cohesion and fell apart while drying.

Color changes were most evident at the surface, bottom and near the column walls, showing some darkening (2.5YR 2.5/2 to 2.5/1), with limited color change in the crushed ortstein. The mixed blueberry leaf extract treated columns had dark coatings in the top layers and near the walls of the columns. Pine treated columns showed only a small color change with some coatings at the very top and bottom of the columns. The columns treated with bracken fern and fescue extract had limited color change with some darker regions at the surface and occasionally at the side. Bent grass and water treated columns did not show significant color variation.

Fungal growth was evident in some columns, particularly with the blueberry columns with and without topsoil. In some columns there appeared to be fungal reproductive structures in the columns and fungal mats in the litter layer. Some recovered ortstein pieces showed fungal growth associated with them. The white pine and water treated columns had some indication of fungal growth. The columns treated with bent grass extract had some fungal material at the bottom.

Some columns became water-logged, ponding water on the surface rather than allowing it to penetrate the crushed ortstein, this was particularly apparent with the fern.

In these cases the columns became anaerobic. Blueberry extract treated columns had decreased permeability and ponding on the surface. Fescue treated columns with topsoil had an anaerobic odor.

The columns with Ap material and rhizosphere material exhibited higher levels of biological activity. The fescue treated columns had many insects, predominantly fruit flies and collembola. Columns with fescue and bent grass rhizosphere material had less leachate passing through the columns. The bent grass grew better than fescue under these conditions, producing more shoot biomass and extensive roots.

Aggregation

All columns that received leaf extract had significantly more aggregation than those that received water (Figure 1). The water columns showed some aggregation in the top layers. All leaf extracts exhibited high aggregation at the surface. The top layer in each treatment showed high levels of aggregation, decreasing downward in the columns. Surface aggregation may reflect compaction and physical changes as well as cementation.

Aggregation in the surface layers (0-3cm) of the extract treated columns were not significantly different, but they were significantly greater than the water treatment ($p<0.05$). The fern extract treatments were significantly less aggregated than the other leaf treatments at the 3-6 cm depth ($p<0.05$), but not significantly different from the water treatment. The difference between fern extract and water treatments at depth remained insignificant. In the top 15 cm of the columns treatments with pine and blueberry extract aggregation was not significantly different. Below 15 cm, it became increasingly different ($p=0.05$). Fescue and bent grass extract treatments were not significantly different in aggregation with depth, except at the very bottom of the column ($p=0.05$).

Podzolizing species such as white pine and blueberry show a more gradual decrease in aggregation, while the depodzolizing species such as bracken fern, bent grass and fescue display a rapid decrease in aggregation. Much of the remaining aggregation observed was associated with dark coatings and the sides of columns. Water treated columns had the lowest aggregation.

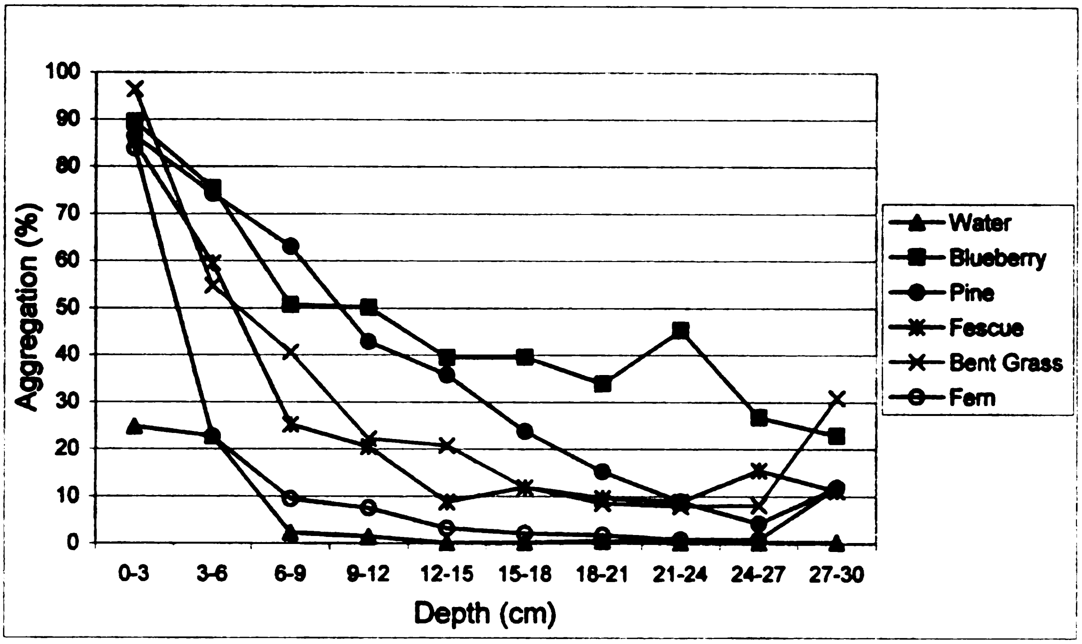

Figure 1. Aggregation (>2mm) with depth for extracts from different plant species.

Tensile Strength of Aggregates

Tensile strength of aggregates was assessed for the uncrushed ortstein and each extract type (Figure 2). Where possible, aggregates at depth were also assessed (Figure 3). Uncrushed ortstein aggregates were crushed as a control for comparison to extract treatments. Aggregate tensile strength differences were significant between treatments and with depth ($p<0.05$). Aggregates from the top layer of the blueberry treatments displayed significantly greater strength than those from pine, fescue and fern ($p=0.05$), but not significantly different than those from bent grass. The strength of aggregates (0-

3cm) treated with blueberry leaf extract was not significantly different from that of uncrushed ortstein aggregates. Within treatments aggregates showed a significant difference with depth from the top layer; below the top layer variability was high. In general the aggregates from uncrushed ortstein and podzolizing species had higher tensile strength than the depodzolizing species. The exception was bent grass aggregates that were not significantly different in strength from pine. There was large variability in the strength of individual aggregates. Some aggregates displayed unusually high tensile strength (twice the standard error); these aggregates often had dark coatings or were associated with column walls. With depth aggregate strength generally decreased, although some of the bottom aggregates showed an increase in strength.

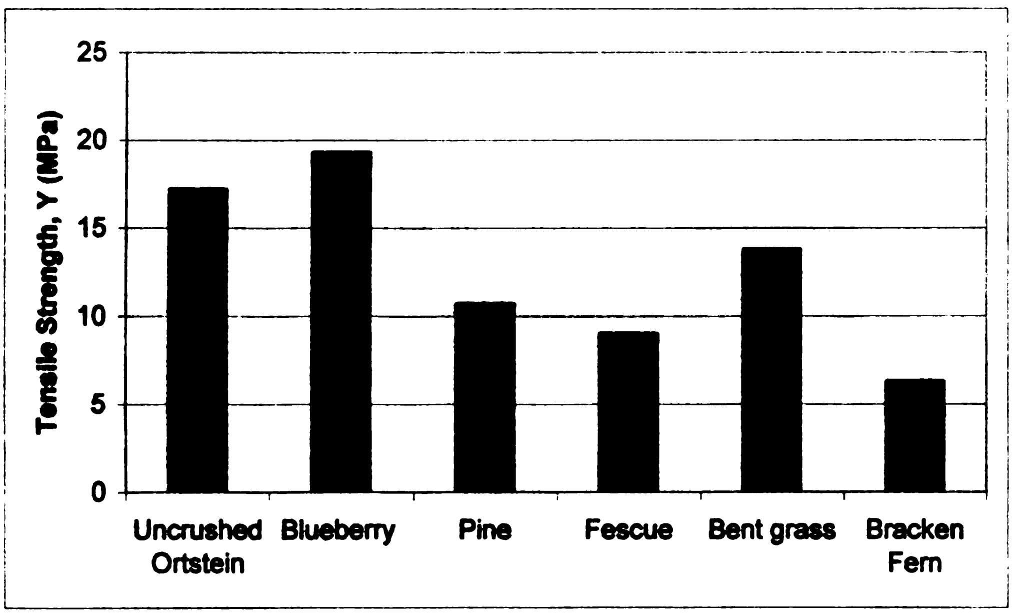

Figure 2. Tensile strength for top layer (0-3cm) receiving extracts from different species.

Because little aggregated material was found in the water treated columns and below 12 cm in most of the other treatments, tensile strength was not determined for those layers. Due to limited amount of aggregated material in the fern and bent grass treatments at depth, tensile strength was not determined.

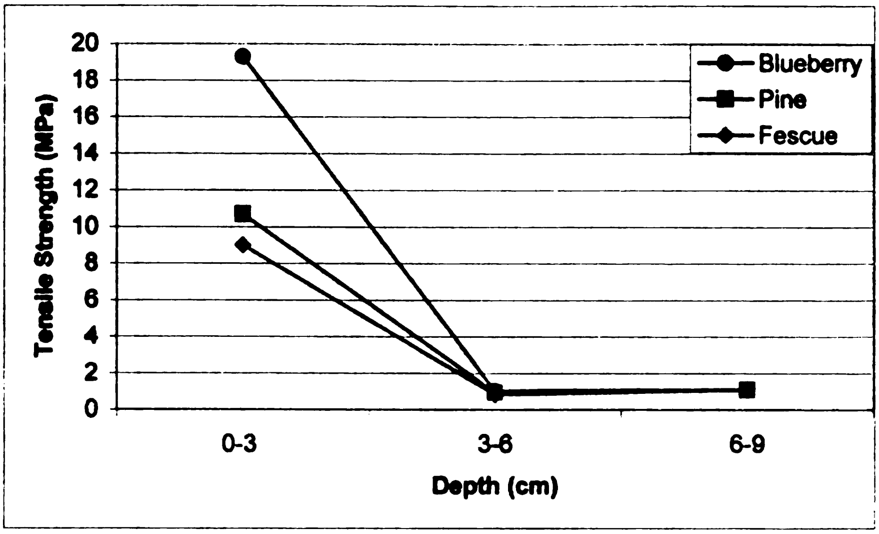

Figure 3. Aggregate tensile strength with depth and different plant species.

The strength of aggregates reflects presence of the cementing agent. It can be affected by preferential flow within the column, wet/dry cycles and crusting. In addition microbial activity may also affect aggregate strength. The differing tensile strength associated with different treatments suggests that some extracts were more effective at inducing cementation than others. High variability in aggregate strength is likely the result of these factors. With increased time, aggregates in lower layers may increase in strength.

Uncrushed Ortstein Pieces

Weight changes of ortstein pieces were determined based on air-dry weights before and after treatment. Blueberry, fescue and white pine had significant increases in weight, while bent grass, fern and water did not have significant changes (Figure 4). The largest force required for crushing was for the control, untreated ortstein (Figure 5). All treatments tended to weaken the ortstein pieces. Blueberry, pine, bent grass and fern treatments were not significantly different from untreated ortstein. The water treatment required the least force for crushing. Fescue extract treatment was not significantly different from the water treatment; both were significantly weaker than the original, untreated ortstein.

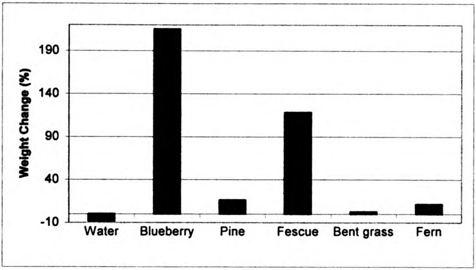

Figure 4. Weight changes for uncrushed ortstein pieces after 12-week leaf extract treatment.

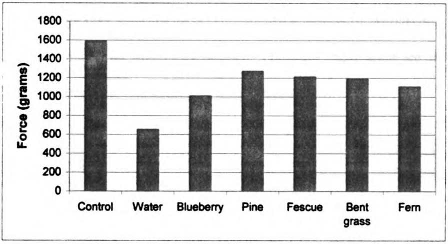

Figure 5. Force required to crush ortstein pieces following 12-week treatment.

Cementing Agents

OM , Al- and Fe- containing compounds have been identified as possible cementing agents in Spodosols. Carbon is associated with organic acids that are able to chelate and transport Al and Fe. Organic acids may be important mechanisms in translocating the Al and acting as a sink for Al in the cemented material. Microbial activity, evidenced by changes in pH and temperature, is able to break down the organic acids, possibly promoting the immobilization of Al and Fe.

Aggregated materials in the top layers of the columns had higher levels of OM and lower Al, while deeper aggregates have lower or similar levels of OM with higher Al (Figures 6, 7 and 8). This suggests that some OM were immobilized at the surface and played a role in the aggregation process there. Higher Al in the aggregated materials at depth suggests that Al-containing compounds are the primary cementing agent in lower layers of the columns. These differences in Al distribution with depth as well as between loose and aggregated materials suggest that Al and Al containing compounds are being transported downward and horizontally in the columns, immobilized and precipitated onto soil particles, thereby cementing the particles.

High OM levels (4.78% OM) are associated with the darkened areas at the cylinder boundaries such as the walls and bottom. These areas are also associated with higher aggregation and aggregate tensile strength.

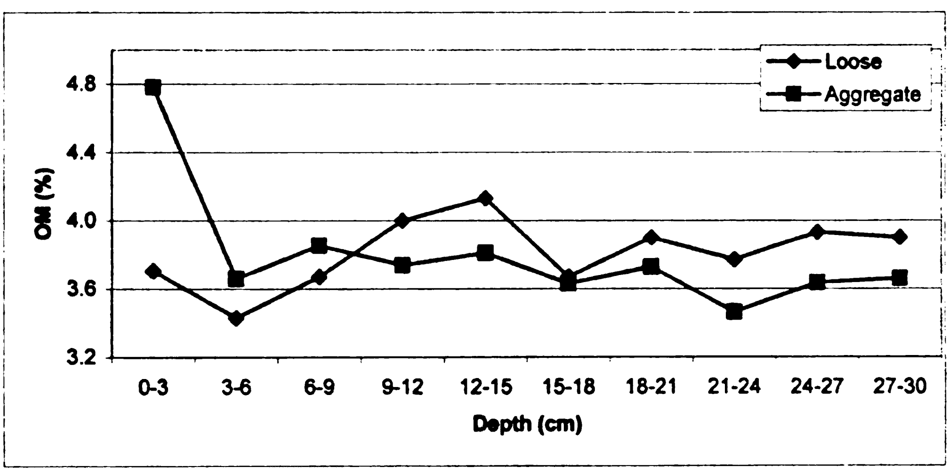

Figure 6. OM in loose and aggregated material with depth after 12-week blueberry extract treatment.

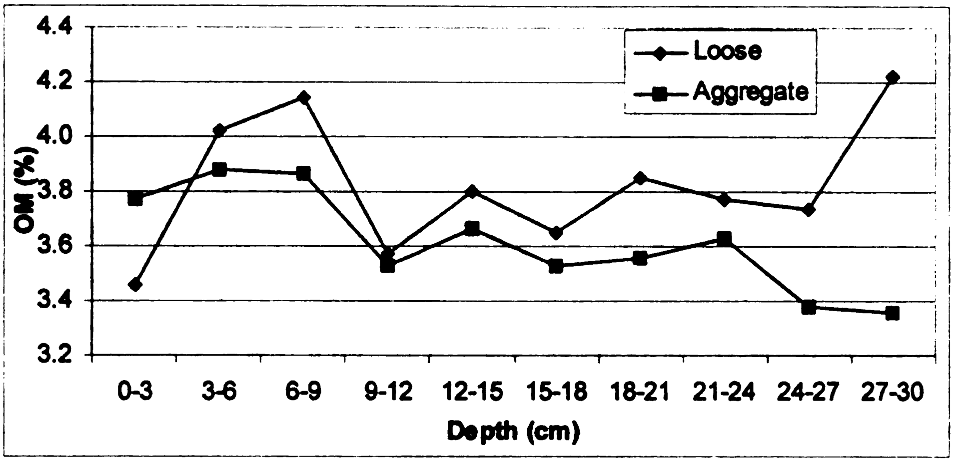

Figure 7. OM in loose and aggregated material with depth after 12-week fescue extract treatment.

Depodzolizing species, bent grass and bracken fern, had lower levels of carbon in the loose material following the 12-week treatment with extracts and less redistribution of Al than podzolizing species. This is consistent with lower levels of aggregation. The OM may have been utilized by microbes, or OM remained soluble and/or was present in the leachate. Bracken fern and bent grass treated columns had lower temperatures than water suggesting that there was no increase in microbial activity. Blueberry, pine and fescue treated columns had higher temperatures than the water treated columns, they also had higher OM and Al, which is consistent with higher aggregation.

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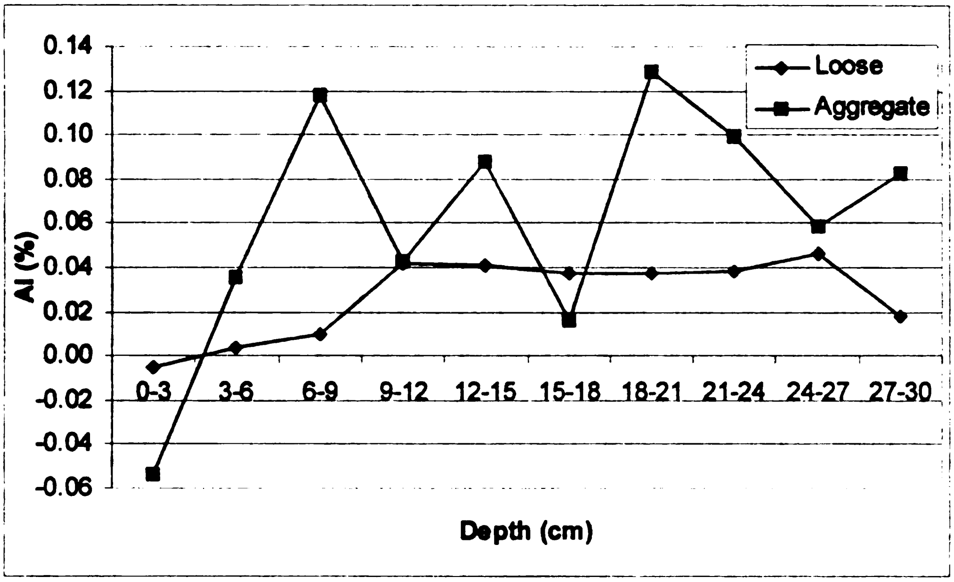

Figure 8. Al distribution changes with depth after 12-week blueberry extract treatment.

The change in Al in the top 3 cm indicates that in the blueberry treatment Al was lost, while at depth Al appears to have accumulated, particularly in the aggregates (Figures 9 and 10). Similarly Al is accumulating at depth in the pine extract treatments. Al was lost in the water and not changed in bent grass treatments.

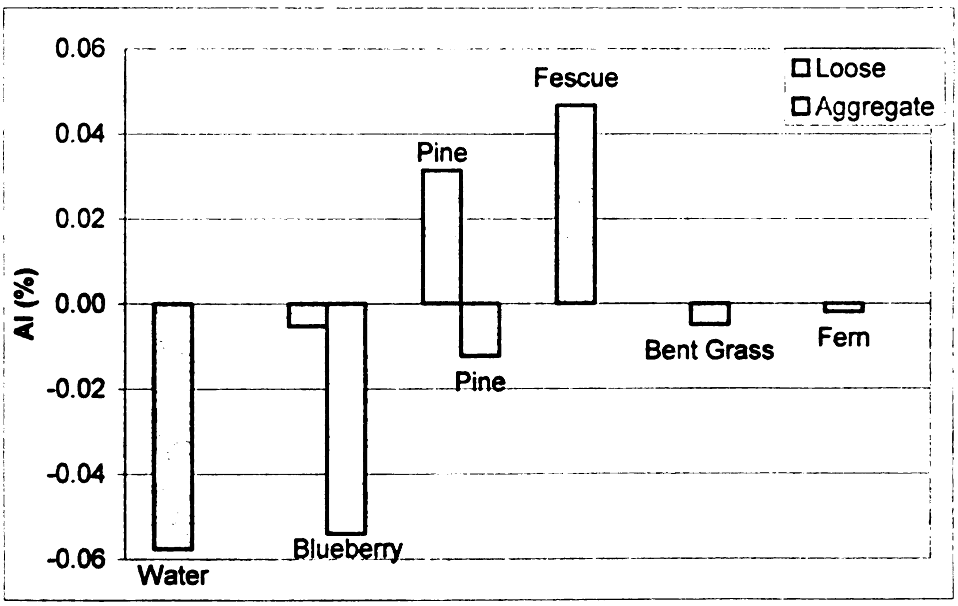

Figure 9. Changes in Al content in the top 3cm of treatment columns.

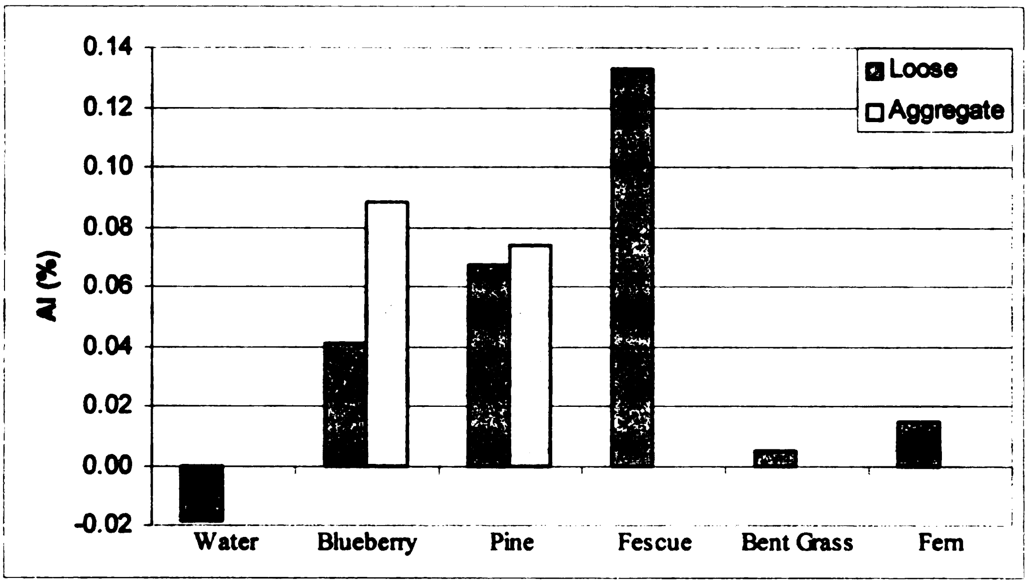

Figure 10. Changes in Al content in the 12-15cm layer of treated columns.

Organic Acids

Leaf extract is a source of organic acids that are able to complex with sesquioxides, mobilize and transport them. Organo-metallic compounds can be degraded by microbial activity and polymerized. These polymers can act as a sink for Al as well as a cementing agent.

In general, the leaf extract of podzolizing species had higher concentrations of LMWOA than depodzolizing species. Blueberry leaf extract most likely contains protocatechuic acid, para-hydrobenzoic acid, gallic acid, catechol and a number of other unidentified LMWOA. This is consistent with higher levels of OM and greater redistribution of Al resulting in increased aggregation. Microbial degradation of the organo-metallic compounds is evidenced by increased temperature and pH changes.

Green blueberry leaf extract showed higher concentrations of organic acids than brown leaf extracts. The amounts and types of compounds present appear to vary with age and the condition of the leaves. The HPLC results support the theory that LMWOA are altered to form higher molecular weight compounds.

Depodzolizing species had lower concentrations of LMWOA than podzolizing species. Fern had several organic acids, most likely gallic acid and catechol, at low concentrations. Fescue and bent grass had low levels of LMWOA, possibly including protocatechuic aldehyde. Low amounts of organic acids in depodzolizing species' leaf extract is consistent with lower pH, temperature, OM and decreased levels of translocation of Al.

pH

Changes in pH are useful indicators of microbial activity and organic acids, as well as an indicator of Al solubility. Podzolizing species had lower leaf extract pH (Figure 11). Aggregated materials had higher pH than loose materials, and upper layers in the columns had increased pH compared to lower layers (Figure 12).

The leaf extract for podzolizing species had higher concentrations of organic acids and lower pH, this is consistent with higher OM and more Al redistribution, resulting in greater aggregation.

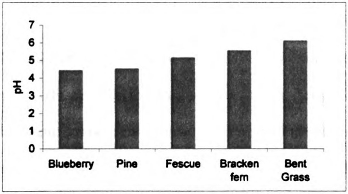

Figure 11. pH of aqueous leaf extract.

Organic acids and organo-metallic complexes are degraded by micro-organisms forming insoluble polymers that act as a cementing agent. During the polymerization of organic compounds from leaf extract there is an increase in pH. The high pH of the top layers is consistent with this polymerization. Aggregated materials deeper in the columns had a significant increase in pH compared to loose material (Figure 12), resulting from the degradation of organo-metallic complexes. The aggregated material also had high Al, this is consistent with decreased Al solubility at higher pH.

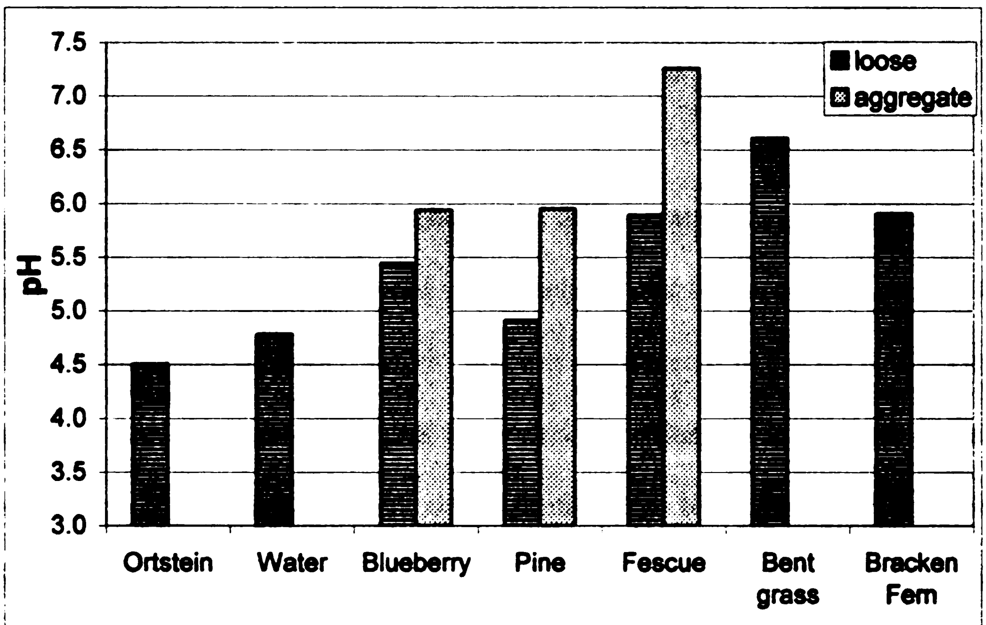

Figure 12. pH of crushed ortstein surface layer (0-3 cm) after 12 week treatment.

Top layers had greater pH increases than deeper layers. Depodzolizing species showed a greater increase in pH of crushed ortstein in the top layer than podzolizing species (Figure 13). This may be a result of higher pH in the extract. The pH of the water treatment was not significantly different from the pH of the original ortstein while all extract treated columns had increases in pH of the top layer.

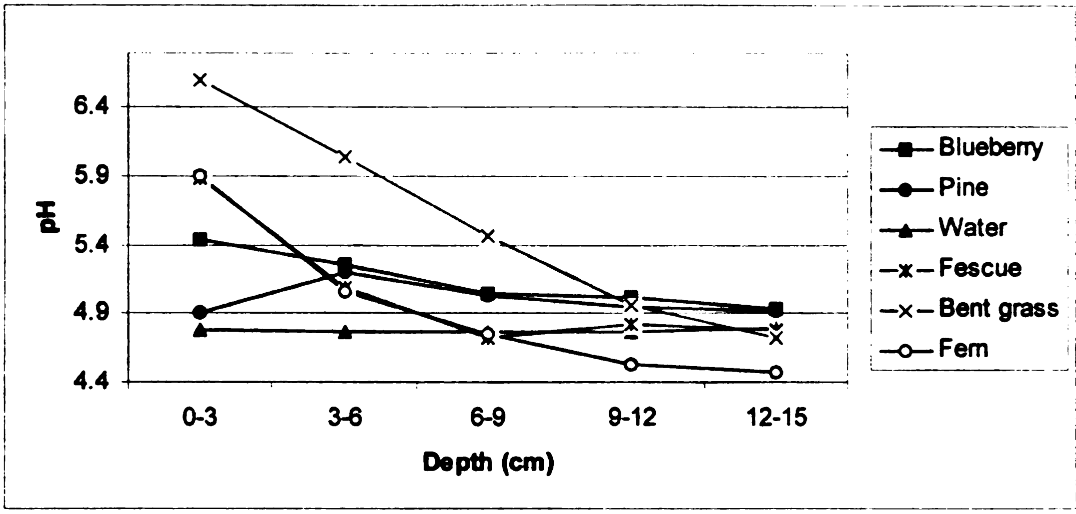

Figure 13. pH of loose materials for extract treatments with depth.

Ap horizon

Columns treated with blueberry and fescue extract containing 2 cm of Ap material were compared to columns treated with blueberry and fescue without Ap soil to assess whether increased microbial activity and organic material in the Ap horizon might effect aggregation. In general addition of Ap material to columns did not cause significant changes in aggregation, pH, Al and OM for fescue or blueberry treatments (Figure 14). Uncrushed ortstein pieces in columns with Ap material did not have a significant difference in weight or strength compared to columns without Ap material. Fescue treatments showed a greater response to the presence of Ap material than blueberry treatments, although they do not tend to be significant or consistent.

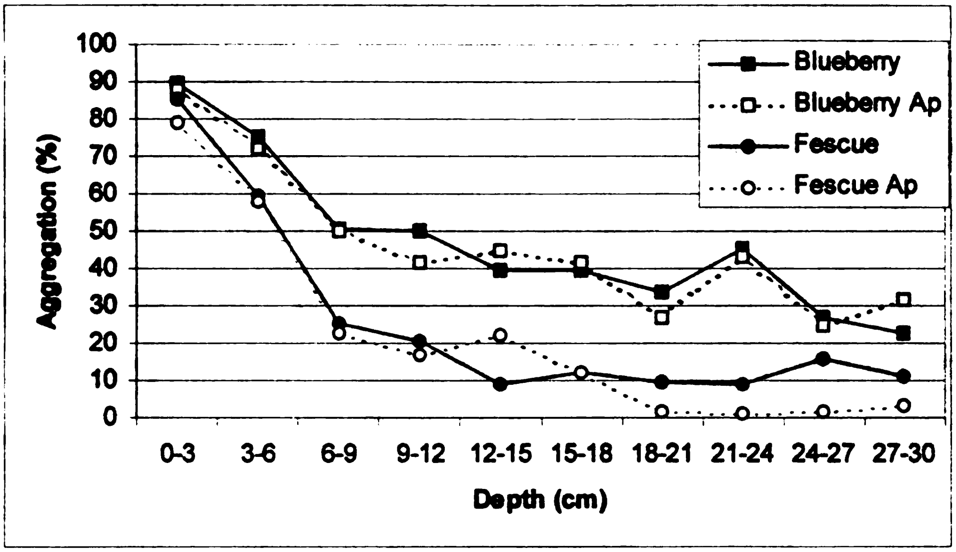

Figure 14. Aggregation (>2mm) with and without Ap material for 12 week blueberry and fescue extract treatments.

Rhizosphere

Rhizosphere columns experienced high levels of biological activity. Root growth was great in columns with bent grass, roots penetrated some of the aggregates. The columns were difficult to analyze as a result of root growth. This root growth may be beneficial in reducing aggregation and breaking up cemented materials.

In rhizosphere columns there were general trends to reduce relocation of Al and changes in pH and OM. This suggests lower levels of aggregation. Ortstein pieces in the columns had less increase in size compared to similar columns without rhizosphere, this was particularly apparent in blueberry leaf extract treated columns.

In bent grass rhizosphere columns treated with bent grass extract ortstein pieces had a decrease in strength, although size/weight increased compared to columns without rhizosphere. In fescue rhizosphere columns treated with fescue extract ortstein pieces had an increase in strength, but no significant change in weight.

Uncrushed ortstein pieces in columns treated with blueberry leaf extract with fescue and bent grass rhizosphere did not show a significant increase in size, although they did have an increase in strength. Uncrushed ortstein pieces in columns treated with blueberry leaf extract alone or with an Ap had significant increases in size. This suggests that the presence of the grass rhizosphere may have inhibited the recementation process.

Temperatures in the rhizosphere columns were generally higher in surface layers with a rapid decrease at depth. The warmer surface temperatures were most likely related to the effects of the grow light, which could have stimulated microbial activity in the area. The use of brown blueberry leaves to make extract may be misleading in the rhizosphere experiments. These factors could be responsible for the lack of carbon accumulation in the surface and translocation of Al that may result in decreased recementation.

The rhizosphere treatments are difficult to evaluate due to the variability of the blueberry extract and its ability to complex Al and the impact of the grow light. The rhizosphere treatment tended to reduce the accumulation of OM in upper layers of columns and reduce translocation of Al, thereby decreasing recementation of crushed ortstein. This is supported by the limited changes of the uncrushed ortstein pieces in the columns.

Blueberry is a strong podzolizer, rapidly increasing aggregation and recementation in crushed ortstein. It is likely that disturbed ortstein recements rapidly following deep tillage in blueberry fields. This may be the cause of reduced plant growth and development.

Depodzolizing species decrease the degree and strength of recementation of crushed ortstein. Rhizosphere experiments had a decrease in the rate of recementation of crushed ortstein when treated with blueberry leaf extract. This suggests that including bent grass between rows of blueberry plants may inhibit the recementation of disturbed ortstein. It may also reduce relocation of Al and encourage the break down of organic acids to reduce the podzolization rate.

CONCLUSIONS

Leaf extract from selected plants had varying ability to recement crushed ortstein. Leaf extract of podzolizing species, blueberry and white pine, had greater ability to recement crushed ortstein than depodzolizing species, fescue, bent grass and bracken fern. Podzolizing species tended to produce stronger aggregates than depodzolizing species.

Ortstein pieces in crushed ortstein increased in weight/size when treated with blueberry leaf extract, however, those treated with bent grass and fern extracts did not significantly change in weight/size.

The addition of topsoil did not significantly effect recementation of crushed ortstein. The addition of rhizosphere decreased the relocation of Al, OM and changes in pH compared to similar columns without rhizosphere. The rhizosphere also decreased the rate of increase of ortstein pieces for blueberry extract treatments.

Since bracken fern is an aggressive pest, bent grass or fescue may be favorable choices to attempt to simulate the natural equilibrium between progressive and retrogressive podzolization. The strong, podzolizing properties of blueberries may be offset with depodzolizing properties of bent grass and its rhizosphere, planted between blueberry rows.

Further studies are needed to assess the types of organic acids associated with blueberries and their role in podzolization. The rhizosphere effect needs to be further evaluated to determine the effect of grow lights in the experiment, along with the effects of ericoid mycorrhizae and blueberry roots in the system and the interaction between species. In addition, long-term field studies should be undertaken to assess the possible use of depodzolizing species to offset podzolization of blueberries. In addition, field studies to better assess ortstein in the field, and changes after trenching and replanting should be evaluated.

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CHAPTER 4

The Influence of Commercial Soil Amendment on the Reformation/Degradation of Disturbed Ortstein

Abstract:

Ortstein formation may inhibit growth in blueberry fields in Michigan. Some growers have used commercially available soil amendments such as Super Symbex 4X to reduce ortstein. This study assessed the effect of Super Symbex 4X on the weight and strength of ortstein pieces when applied at different rates, and its ability to reduce the recementation of crushed ortstein by blueberry leaf extract. Columns contain crushed ortstein and ortstein pieces were treated for 12 weeks with water and Super Symbex 4X at the suggested rate, 10 and 100 times the suggested rate, and Super Symbex 4X with blueberry leaf extract. Changes in weight and strength of the ortstein pieces were determined. Super Symbex 4X and water treated ortstein pieces did not show a significant difference in the strength or size. Symbex treatment with aqueous blueberry leaf extract did show a significant decrease in the recementation of crushed ortstein compared to blueberry leaf extract treatment alone, although there was not a significant effect on the strength of the uncrushed ortstein. Super Symbex 4X may be useful in inhibiting or retarding the recementation of disturbed ortstein in blueberry fields following deep tillage.

INTRODUCTION

Blueberries are known to encourage podzolization in soils (Dimbleby and Gill, 1955; Miles, 1985; Mokma and Buurman, 1982). Cementation of B horizon materials can occur rapidly, recent laboratory studies indicate that cementation can be initiated in less than 1½ weeks in crushed ortstein materials (Chapter 2). Rapid recementation of disturbed ortstein rapidly diminishes the advantage of deep tillage to break up Bhsm materials and improve soil penetration by water and roots.

Commercially available soil amendments claim that they can reduce soil hardpan. Ortstein is frequently referred to as hardpan. These amendments have not been scientifically proven to decrease the ortstein in blueberry fields. Agro-K produces Super Symbex 4X, a "microbial enzyme and metabolic activator developed through the fermentation of several microbes and micronutrients" (http://www.agro-k.com/agronomy/main_agro_frm.htm). Agro-K states that after application of Super Symbex 4X in citrus crops there was a notable change in the depth to the hardpan, however, the type of hardpan was not specified. The amendment stimulates natural bacteria and the bacterial activity breaks up the hardpan. It was suggested that the product would require 3-5 years to break up hardpan (Larry Shaffer, 7 July 2000, personal communication).

The objectives of this study were to assess 1) the effect of Super Symbex 4X on the weight and strength of ortstein pieces when applied at different rates and 2) the ability of Super Symbex 4X to reduce the recementation of crushed ortstein by blueberry leaf extract.

MATERIALS AND METHODS

Ortstein samples were collected from the study area in a blueberry field near West Olive, MI; the soil is Saugatuck sand (Typic Durorthod, sandy, mixed, mesic). A trench was dug and Bhsm horizon material extracted from the sidewalls. The material was then air dried, crushed and passed through a 2.0 mm sieve. Some uncrushed ortstein pieces, approximately 10g, were collected for use in the study.

Blueberry leaves were collected from blueberry plants as well as under the plants, cleaned and stored at 5°C. Extract solutions were prepared fresh weekly by placing crushed leaves in distilled water at a 1g:10 ml ratio. This mixture set for 24 hours at 20°C. The extract was filtered usng a Buchner funnel and stored at 5°C.

Cylindrical, plexiglass tubes 30 cm in length and 11.5 cm inside diameter were mounted vertically. The bottom was held with cheesecloth. Crushed ortstein material was placed in the columns. Five air-dried, pre-weighed pieces of uncrushed ortstein were added to each column.

Blueberry leaf extract or water was applied daily at a rate of 20 ml, this is approximately twice the rate of precipitation in the region. Super Symbex solution was added at 45-day intervals using the recommended rate (1 qt/acre) as well as 10 and 100 times the recommended rate.

At the end of the treatment period columns were allowed to air dry. The ortstein pieces were air dried and weighed for comparison to original weights. Structural tensile strength was also assessed by an aggregate crushing technique (Dexter and Kroesbergen, 1985; Smucker, 2001, personal conversation). Only the actual force required to break the peds was used, owing to size changes in the original peds. Additional material on some of the peds formed hybrid structural units with varied tensile strengths. The force values were compared to those of the original ortstein.

Data from this study were analyzed using Mixed model procedure (Proc mixed) with repeated statement in SAS statistical software. The logarithmic transformation was applied to weight and strength data to provide normality assumption for analysis. Differences between treatments were determined by using least squared means (LSMEANS) differences in the ($p<0.05$) significance level with the Tukey-Kramer adjustment.

RESULTS AND DISCUSSION

Columns treated with blueberry extract were very firm and cohesive, with areas of dark coatings (2.5YR 2.5/1 and 2.5YR 2.5/2) compared to the remainder of the uncrushed ortstein (2.5YR 2.5/3). The water treated columns had very little or no cohesion and no color change from the original crushed ortstein 2.5YR 2.5/3). The Symbex treated columns were less cohesive than those treated with blueberry extract alone and did not have the dark coatings.

Ortstein pieces treated with Super Symbex at 1x and 10x decreased in size (Figure 1), however they increased in size with 100x treatment. This may be a response to increase carbon in the system with high levels of Symbex. Ortstein pieces treated with a combination of blueberry leaf extract and Super Symbex 4X were not significantly different in size from water or Symbex treatments. The Symbex may have been able to activate microbial activity and decompose organic compounds before they were able to translocate the Al. Weight changes for Symbex treatment were not significantly different from water treatments. Ortstein pieces treated with blueberry extract alone were significantly larger than those treated with blueberry extract plus Symbex or Symbex plus water. This also suggests that the Symbex was able to retard the translocation of Al in the columns and prevent the reformation of ortstein.

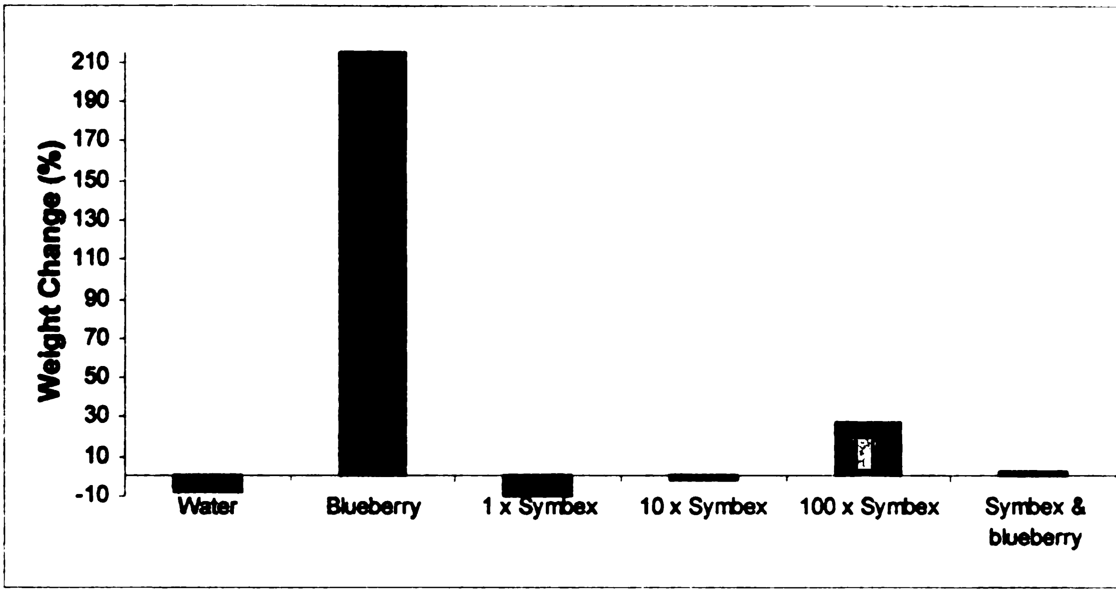

Figure 1. Weight changes of the ortstein pieces placed in crushed ortstein and treated for 12 weeks.

Ortstein pieces treated with a combination of blueberry and Symbex were not significantly different in strength than those treated with blueberry extract alone (Figure 2), but were stronger than those treated with water or Symbex plus water. Log values of force required to deform uncrushed pieces of ortstein treated with Symbex were not significantly different from water treatments. The control, uncrushed ortstein was significantly stronger than all of the treatments.

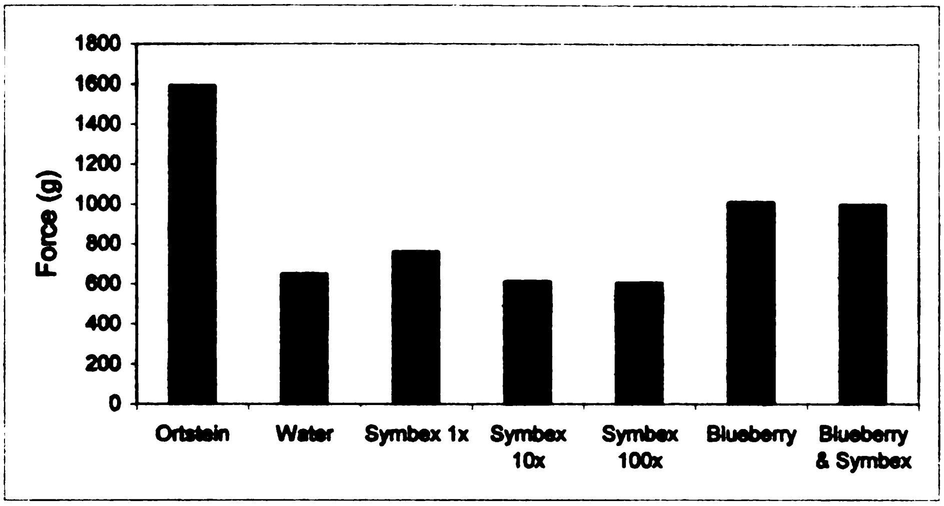

Figure 2. Force required to crush ortstein pieces.

The pH values of soil treated with Symbex increased when compared to water or blueberry treatments. Symbex treatments tended to have less leachate.

Super Symbex 4X significantly reduced the recementation of crushed ortstein. Application of Super Symbex 4X at the recommended rate may inhibit recementation of crushed ortstein in soil with blueberries. However, strength of uncrushed ortstein did not appear to be effected by the treatment. The results of this study suggest that Super Symbex 4x may help prevent recementing of ortstein broken by deep tillage for blueberry production.

CONCLUSIONS

At the recommended rate and 10x Super Symbex 4X reduced the weight and strength of ortstein pieces, at 100x the recommended rate there was an insignificant increase in size and decrease in strength. Super Symbex 4X was able to reduce the rate of recementation of crushed ortstein when used with blueberry extract. This suggests that it may be useful in inhibiting the recementation of disturbed ortstein in blueberry fields following deep tillage.

Future studies to evaluate the effectiveness of Super Symbex 4X with blueberry plants and with other species may help to develop a mixed system in which the ortstein formation is balanced by the regressive podzolization of other species to maintain a sustainable system. Further studies are recommended to assess the role of Super Symbex 4X in blueberry fields. The quality of leaf litter and its ability to affect podzolization (Bronick, Chapter 3) suggests that studies on Symbex used with fresh blueberry leaf extract would help to better understand the ability of Symbex to decrease recementation of disturbed ortstein. The effect of Symbex in the presence of soil microorganisms and the affect of rhizosphere on recementation of crushed ortstein should also be studied.

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CHAPTER 5

Aggregation of Crushed Ortstein by Selected Organic Acids

Abstract:

Four organic acids identified in the plant extracts were used to evaluate their ability to bind crushed ortstein particles together. The purpose of this study was to assess the ability of selected organic acids to aggregate crushed ortstein and evaluate the effect of adding a commercial soil amendment, Super Symbex 4X. Solutions of protocatechuic acid (PCA), ρ-hydroxybenzoic acid (ρHBA), catechol and vanillic acid (VA) were added to crushed ortstein. Super Symbex 4X was added to the crushed ortstein and mixed with the organic acids at the suggested rate. After 5 weeks the mixtures had visible changes in color, aggregation and microbial activity. The water control and catechol did not show high levels of aggregation, although they did have microbial activity and color changes. PCA, ρHBA and VA showed high levels of aggregation. Addition of Super Symbex 4X to the mixtures decreased aggregation with the strongly aggregating organic acids, PCA, ρHBA and VA. Aggregation increased in Super Symbex 4X treatments with weakly aggregating solutions such as, catechol and water.

INTRODUCTION

Organic acids possibly involved in the podzolization process were identified from the literature. Protocatechuic acid (PCA) has been identified as a possible mechanism for the translocation of sesquioxides in Spodosols in Michigan (Vance et al., 1986). Protocatechuic acid can be a degradation product of ρ-hydroxybenzoic acid (ρHBA) and vanillic acid (VA) (Vance et al., 1986). These organic acids were present in fresh blueberry leaf extract. Catechol was found to be present in large quantities in 2-week old blueberry leaf extract (Chapter 2).

The purpose of this study was to assess the ability of selected organic acids to aggregate crushed ortstein and evaluate the effect of adding Super Symbex 4X.

MATERIALS AND METHODS

Organic acid solutions (0.005g:100ml distilled water) were added to a 5g sample of crushed ortstein in a 200 ml conical flask. The ortstein had been passed through a 2 mm sieve. Water and water with Super Symbex 4X and crushed ortstein were used as controls. The mixtures were allowed to stand for 5 weeks at room temperature.

At the end of the treatment, the solutions were decanted and the crushed ortstein was air dried and then sieved. The air dry weight of the loose material and aggregated (remained on 2mm sieve) were compared. OM was determined by loss-on-ignition (Schulte, 1988) and pH was determined (Soil Survey Staff, 1984).

RESULTS AND DISCUSSION

The PCA, VA and ρHBA treatments had large amounts of aggregation and catechol and water treatments had lesser amounts (Figure 1). The amounts may be less than actual aggregation because much of the material clung to the container and some broke up during transfer. Aggregation is possibly a result of organic acids complexing with Al and transporting the Al to particles, as the organic ligands degraded and polymerized organo-metallic compounds would cement particles together. PCA had the greatest aggregation. This is consistent with findings (Vance et al., 1986) that PCA appears to play a role in podzolization. PCA was found in high concentrations in B horizons with more Al, suggesting that PCA played a role in the Al mobility. PCA has a strong ability to complex with polyvalent cations such as Al because it has 2 juxtaposed hydroxyl functional groups that are able to strongly bond to polyvalent cations. This organo-metallic complex remains mobile and transports Al. Microbial degradation of the organic ligand is a possible mechanism for the immobilization and precipitation of Al. Organo-metallic complexes are polymerized and become immobile. The organo-metallic polymers can act as a cementing agent as well as bridging of Al cations. In treatments with little aggregation, such as water and catechol, microbial activity from the Symbex may not have played a role in Al related cementing of particles, however microbial organic compounds may have had a role in cementing particles.

Some color changes were visible; small, dark masses were particularly visible in catechol and ρHBA treatments. Very little microbial activity was visible. OM in aggregated materials tended to be higher than in loose material for all treatments including water, with the exception of VA where OM remained constant. pH for loose materials was similar for all treatments, ranging from 4.5-4.6, there was insufficient material to determine the pH for aggregated materials.

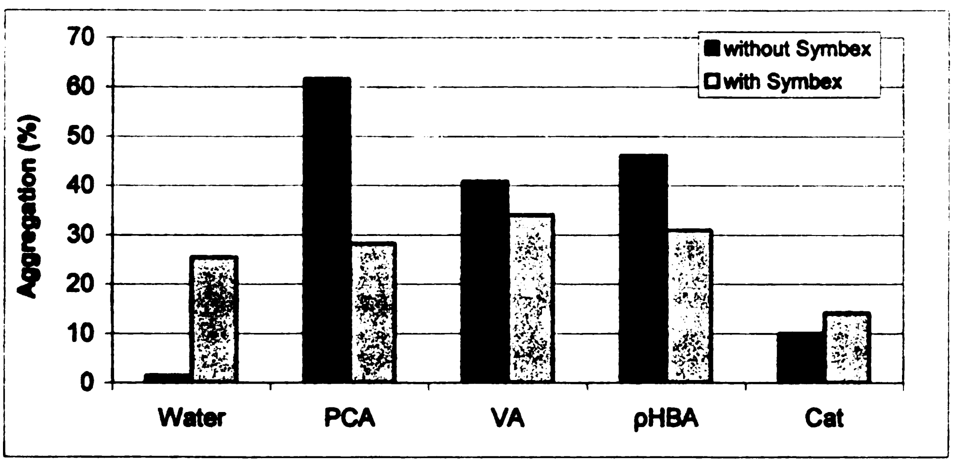

Figure 1. Aggregation of crushed ortstein for selected organic acids (protocatechuic acid, vanillic acid, ρ-hydrobenzoic acid and catechol) with and without Super Symbex 4X.

Organic acids/water treatments displaying less aggregation, such as water and catechol, tended to have higher aggregation in the Symbex treatments than without Symbex. Organic acid solutions resulting in higher aggregation, such as PCA, ρHBA and VA treatments, had a decrease in aggregation in the Symbex treated samples.

Crushed ortstein samples mixed with organic acid solutions and Symbex tended to have higher pH (5.2) than soil solution mixtures without Symbex (4.6), with the exception of catechol which remained constant. This may be a result of microbial degradation of organic acids, raising the pH. Loose materials treated with Symbex treatments had similar OM (3.8%) and higher pH (5.3) than those not receiving Symbex treatments (OM =3.7%, pH=4.6). Aggregated materials in Symbex treatments had lower OM (3.5%) than untreated samples (5.0%).

The Symbex treated samples, including water without an organic acid, showed higher levels of microbial activity, evidenced by blooms of microbial mass.

The addition of Symbex increased the OM and pH in loose materials while aggregated materials had less OM. At higher pH Al is less soluble. Aggregation may be inhibited by Symbex. The increased microbial activity associated with Symbex may breakdown the organic acids, consuming OM and preventing complexation with Al.

CONCLUSIONS

The organic acids were able to aggregate crushed ortstein at varying levels, with PCA > ρHBA > VA > catechol. Super Symbex 4X was able to decrease aggregation in strongly aggregating organic acids. Further studies are suggested to assess the organic acids that are present in blueberry leaf extract and compare them to depodzolizing species leaf extract as well as to evaluate the changes in organic acids through the season along with changes as the acids degrade.

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CHAPTER 6

Podzolization in Pit

Abstract:

A pit resulting from removal of soil material for highway construction, was studied to evaluate how quickly evidence of podzolization was apparent. The purpose of this study was to assess podzolization under two tree species planted on C horizon material and compare the effect of these tree species to barren parent material. E, Bs and C horizon materials under Jack pine and Red pine were analyzed for OM by loss-on-ignition, Al and Fe by ammonium oxalate extraction and plasma emission spectroscopy, pH and color. Soil colors indicated the presence of eluvial and illuvial processes. OM and pH of the soils showed surface increases while Al and to a lesser extent Fe showed indications of translocation. After approximately 40 years of soil formation the soils exhibit evidence of podzolization.

INTRODUCTION

During formation of soil, parent material is modified by interactions of vegetation, climate and topography over time to develop soil horizons. The rate of soil development is difficult to assess because of the extended time involved and changes in vegetation due to natural succession. Many chronosequences do not include young soils. The unique nature of this study relies on the exposure of parent material in situ with controlled plantings and about 40 years of exposure to soil-forming processes.

The study area is a 6-acre soil pit in the Houghton Lake State Forest (White, 1965). Soil material was removed for construction of highway US-27 prior to 1960, exposing the C horizon in the pit. The soil in the adjacent soil map unit is Rubicon Sand

(Entic Haplorthod, sandy, mixed, frigid). Experimental tree planting trials were established in 1960 to assess the effectiveness of fertilization treatments in the reforestation of areas with nutrient-deficient soils (White, 1965). Several conifers were planted in randomized block design including red pine (*Pinus resinosa* Ait.) and jack pine (*Pinus banksiana* Lamb.). The fertilization treatments influenced the initial reforestation, they are not likely to influence soil formation. The tree plantings provide an opportunity to study early stages of soil development.

The purpose of this study was to determine if podzolization was evident visually or chemically after 40 years of soil formation under two tree species planted on C horizon material. This was accomplished by evaluating morphological and chemical changes in the parent soil material in the pit and comparing that to associated soil that formed out of the pit.

MATERIALS AND METHODS

Samples of E, Bs and C horizons were collected from 6 pedons in jack and red pine plots. Samples were also collected from the A, E, Bs, BC and C horizons from two pedons in undisturbed soil approximately 50 feet east of the pit. Soil colors were determined from 30 pedons in the pit.

Soil samples were analyzed for C, Al, Fe and pH. OM content was determined using the loss-on-ignition (LOI) method (Schulte, 1988). Al and Fe were extracted with ammonium oxalate (Soil Survey Staff, 1984). The extract was analyzed by direct coupled plasma emission spectroscopy (DCP) for Al and Fe content and with a spectrophotometer for optical density of oxalate extract (ODOE). Samples were analyzed for pH using a 1:1 soil:water ratio.

Data from this study were analyzed using Mixed model procedure (Proc mixed) with repeated statement in SAS statistical software. The logarithmic transformation was applied to Al, Fe, OM and pH data to provide the normality assumption for analysis. Differences between treatments were determined by using least squared means (LSMEANS) differences in the ($p<0.05$) significance level.

RESULTS AND DISCUSSION

The color of E horizons from both jack and red pine plots had lower chroma than C horizons (Table 1) indicating removal of Fe oxide coatings. The Bs horizons had lower values and higher chroma than C horizons indicating the accumulation of humus and sesquioxides. The E horizons of the well developed, control pedons had similar colors, however, the B horizons had a redder hue suggesting greater accumulation of OM, Al and Fe than in the pit horizons. These color changes indicate that eluvial processes have occurred in the E horizons and illuvial processes have occurred in the B horizons, with OM, Al and Fe concentrations increasing in the B horizons.

Table 1. Color of horizons formed under Red Pine and Jack Pine in the pit and the control outside the pit.

Horizon Colors			
Horizon	Red Pine	Jack Pine	Control
E	10 YR 6/2	10 YR 5-6/1-2	10 YR 6/1-2
Bs	10 YR 4-5/3-4	10 YR 4-5/4-6	7.5 YR 4/4
C	10 YR 6/3	10 YR 6/3	10 YR 6/4

Al and Fe

Translocation of Al was evident from lower levels in E horizons and increased levels in Bs horizons compared to C horizons (Figure 1). Under jack pine there was more Fe in Bs horizons than E horizons indicating translocation of Fe in these pedons (Figure 2). There was no evidence of translocation of Fe in the soils under red pine.

The mobilization of Al and Fe likely resulted from decreased pH in the surface layer thereby increasing the solubility of Al and complexation with organic acids from plant materials complexing sesquioxides and transporting them deeper in the soil profile. As organic ligands are exposed to microbial decomposition and increased pH at depth, Al is released and precipitated.

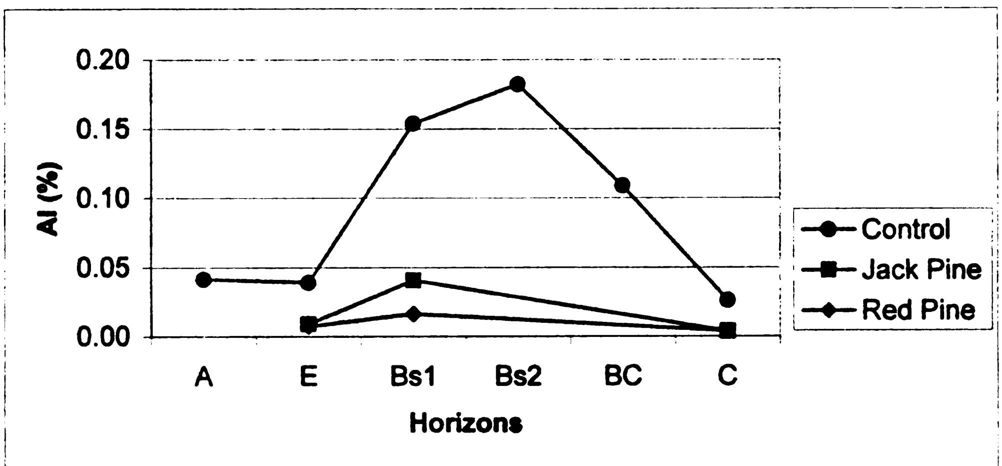

Figure 1. Al concentrations in pit and control outside pit with depth.

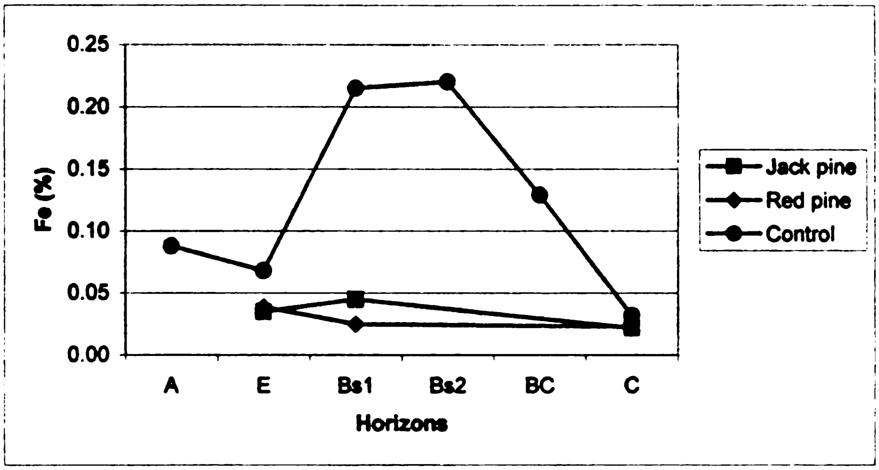

Figure 2. Fe concentrations in pit and control outside pit with depth.

The pit samples had a decrease in pH in the upper horizons, the effect decreasing with depth (Figure 3). Plant uptake of nutrients contributes to the decrease of pH at the surface. The pH is further affected by the addition and decomposition of organic matter. Red pine litter appears to be more acidifying than jack pine litter. This may be related to the tendency of jack pines to hold their needles and branches longer than red pine, and thereby supply less fresh organic matter to the soil. The control samples taken outside the pit had lower pH values in the upper horizons.

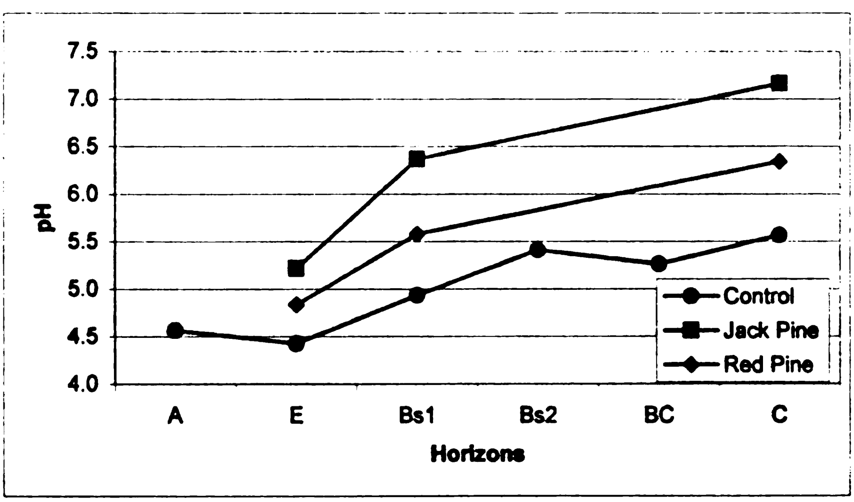

Figure 3. pH for soil horizons under Jack and Red pine trees in the pit and the control soil near the pit.

Surface layers of pedons from the pit had more OM than the C horizon (Figure 4). This is consistent with the presence of vegetation and formation of an A horizon. OM tends to be moved from the E horizons to the Bs horizons more in jack pine than in red pine. The average ratio of OM in the E:Bs was higher in red pine (1.6) than in jack pine (1.1).

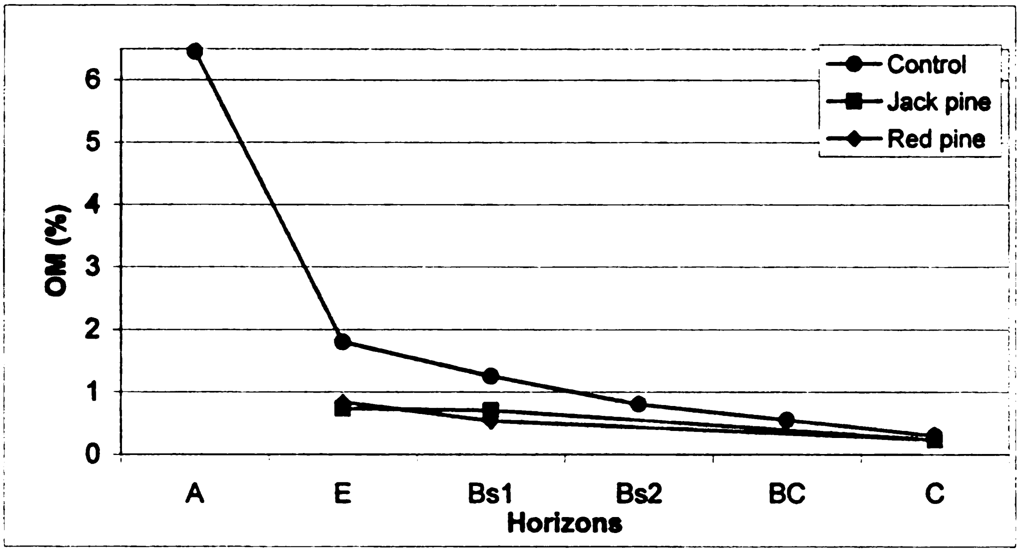

Figure 4. OM in soil horizons under Jack and Red pine trees in the pit and control soil near the pit.

Soil development is heavily influenced by vegetative growth, which contributes OM through leaf litter, stem flow, root exudates and increased soil microbial communities and their effects. This is consistent with the increase in OM in the upper layers of the pit materials. Soil fauna including microorganisms, arthropods and other macroorganisms, contribute to the decomposition of organic matter and release of organic substances. Earthworms and other soil organisms contribute to the mixing of organic matter from the surface deeper into the soil profile. These all contribute to the increase in OM at the surface and decrease of pH.

Optical density of oxalate extract (ODOE) has been found to be a good measure of OM that is involved with translocation of Al and Fe (Mokma, 1993). ODOE values were highest in Bs horizons and lowest in C horizons (Table 2). This trend was stronger in the jack pine than in the red pine. This is consistent with the soil under jack pine having more translocation Al and Fe.

Table 2. ODOE values for pit and control horizons.

ODOE			
Horizon	Red Pine	Jack pine	Control
E	0.22	0.13	0.41
Bs	0.21	0.30	0.69
C	0.07	0.10	0.11

Alterations in physical soil parameters tend to be apparent over longer periods of time whereas chemical characteristics can be apparent in a shorter time period. The use of pH, OM, Al and Fe as early indicators of Spodosol development and podzolization following the exposure of C horizon materials is appropriate for monitoring the rate of soil formation.

CONCLUSIONS

Forty years after soil removal and planting of conifers, podzolization had formed a weakly developed soil. Addition of organic matter and translocation of OM, Al and Fe are the major processes that have formed the soil.

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CHAPTER 7

Conclusions

Blueberry extract can rapidly promote aggregation in crushed ortstein; aggregation was apparent in 1½ weeks. The rate and strength of aggregation appear to be dependent on the quality of the extract. Fresh blueberry leaf extract had high levels of low molecular weight organic acids (LMWOA). High concentrations of LMWOA, specifically organic acids which are better able to bond with Al such as protocatechuic acid (PCA), ρ-hydroxybenzoic acid (ρHBA) and vanillic acid (VA), tend to increase the rate of aggregation and translocation of Al. In the upper layers of the crushed ortstein organic matter (OM) played an important role in forming aggregates and Al was eluviated while deeper in the columns Al was immobilized and was important in the formation of aggregates. High levels of organic acids are consistent with higher concentrations of OM, less increase in pH and higher temperatures as a consequence of microbial degradation of the organic acids and the ensuing release and precipitation of Al at depth in the columns compared to depodzolizing species. Chemical processes such as chelation of Al by organic acids leads to physical changes including the relocation of Al to contact points between particles, which acts as a bonding agent.

The presence of depodzolizing species such as bracken fern and bent grass, including the rhizosphere, resulted in less translocation of Al and recementation of crushed ortstein. Extracts of depodzolizing species decreased the rate of increase in weight of the ortstein pieces in columns. This may be related to lower levels of LMWOA available to complex and translocate Al. The increased pH at the surface of these columns is consistent with decreased Al mobilization. These results suggest that the use of depodzolizers in blueberry systems may decrease the rate of reformation of disturbed ortstein.

Application of Super Symbex 4X to columns of crushed ortstein reduced the rate of reformation of ortstein pieces. This may further reduce the rate of reformation of disturbed ortstein. The addition of Super Symbex 4X to organic acid solutions with crushed ortstein indicates that it interferes with the complexing and aggregating ability of some organic acids.

A combination of deep tillage to breakup ortstein, along with the use of Super Symbex 4X and companion planting with a depodzolizing species such as bent grass, may offset the strong podzolizing properties of blueberries and inhibit the reformation of ortstein. This may enable blueberry replants to mature and produce in regions of inhibited growth and development.

The use of raised beds in blueberry fields may decrease penetration of water carrying organic compounds into the zone of broken ortstein. The increased thickness of Ap horizon material would improve surface drainage and decrease aeration concern. Utilizing Ap material that has already undergone eluvial processes would decrease Al available for translocation. Surface runoff from the raised beds would flow from the row into the inter rows with depodzolizing plants such as bent grass. The combination of reducing the penetration of water carrying organic acids, redirection of this surface solution to mid row with depodzolizers, thicker Ap horizon made from Ap material from which some Al has already been removed, results in less water carrying organic acids penetrating the soil, complexing with Al and translocating it. This results in less recementation.

Compost may be beneficial in increasing microbial activity, breaking down organic acids before they penetrate into the broken ortstein. Therefore, there are less organic acids available to complex and transport Al. This may also increase the pH of the Ap horizon, allowing for less mobilization of Al.

Appendix A

Blueberry Field Study Data Tables

Table A.1. Aggregation (%*) after blueberry leaf extract addition.

Extract	Blueberry						
Leaf color/ Treatment	Green			Brown			
Time (wk)	1 1/2	3	6	1 1/2	3	6	9
Depth (cm)							
0-3	96.1±3.4	95.9±0.1	99.5±0.9	37.9±8.6	73.2±3.7	69.5±8.3	60.5±7.2
3-6	75.4±7.0	65.0±2.4	86.5±11.7	10.4±2.9	30.6±5.3	35.7±15.7	33.2±4.5
6-9	63.0±2.1	56.7±5.8	81.3±9.4	1.9±0.4	16.5±4.9	12.6±0.6	24.2±3.1
9-12	54.4±5.0	56.2±3.5	74.8±4.6	1.6±0.8	11.7±2.1	12.9±4.7	19.9±11.7
12-15	57.0±21.3	64.4±11.5	81.3±10.1				

* % remaining on 2mm sieve.

Table A.2. Aggregation (%*) after treatment.

Extract	Blueberry			Pine	Fescue		Bent Grass	Fern	Water
Leaf color/ Treatment	Mixed		Mixed, Ap			Ap			
Time (wk)	12	21	12	12	12	12	12	12	12
Depth (cm)									
0-3	89.5±2.8	86.7±11.5	87.6±4.3	86.4±7.3	85.1±11.1	79.2±13.9	96.3±1.5	83.8±4.2	24.8±5.9
3-6	75.4±7.9	70.5±9.3	72.1±5.2	74.2±6.5	59.5±2.5	58.0±7.6	54.8±7.2	22.6±2.7	22.7±4.2
6-9	50.6±13.9	51.4±4.5	50.2±17.1	63±9.8	25.2±8.2	22.5±10.2	40.5±13.1	9.4±2.4	2.2±1.4
9-12	50.1±10.7	56.8±3.7	41.7±7.4	42.8±6.3	20.5±2.9	17.1±12.2	22.2±5.0	7.5±4.7	1.5±0.3
12-15	39.4±14.1	54.3±3.7	44.9±16.3	35.8±11.0	8.8±5.6	21.9±5.7	20.8±13.8	3.2±3.0	0.1±0.1
15-18	39.5±9.7	50.6±15.1	41.7±9.1	23.7±10.5	11.9±6.5	12.2±4.5	11.9±6.9	2.1±1.6	0.2±0.2
18-21	33.9±11.9	52.7±13.7	26.6±3.3	15.2±8.6	9.6±5.8	1.3±0.7	8.5±9.0	1.8±0.7	0.6±0.1
21-24	45.3±15.1	49.9±4.2	43.3±7.5	8.8±6.7	8.8±6.1	0.8±0.7	7.9±3.5	0.8±1.0	0.2±0.1
24-27	26.8±12.5	35.7±4.6	25±15.7	4.2±4.1	15.6±10.5	1.5±1.8	8.1±0.4	0.8±0.7	0.2±0.1
27-30	22.9±10.7	28.3±8.1	31.4±33.7	11.8±9.6	11.2±9.8	3.1±3.3	30.9±2.3	11.9±8.5	0.3±0.1

* % remaining on 2mm sieve.

Table A.3. Tensile Strength (MPa)

Extract	Blueberry							Pine	Fescue	Bent	Bracken	Uncrushed
	Green			Brown						Grass	Fern	Ortstein
Time (wk)	1 1/2	3	6	1 1/2	3	6	12	12	12	12	12	
Depth (cm)												
0-3	4.32±3.5	5.64±5.4	11.51±7.3	0.37±0.01	1.77±0.7	2.63±1.2	19.34±22.9	10.7±7.6	9.0±5.1	13.8±11.3	6.27±5.1	17.2±5.5
3-6	1.21±0.8	1.6±1.3	6.42±4.5				1.03±0.78	0.95±0.7	0.83±1.2			
6-9	0.88±0.6	1.41±1.1	2.91±1.9				1.1±1.0	1.11±0.5	1.11±1.3			
9-12	0.75±0.3	1.09±0.7	2.71±1.8				1.05±0.6	1.19±1.4				
12-15	0.65±0.3	0.64±0.5	1.41±1.2				0.62±0.3	1.25±1.0				
15-18							0.57±0.8	1.02±0.5				
18-21							0.60±0.6	0.61±0.8				
21-24							0.83±0.6					
24-27							0.76±0.8					

*n=30
± Standard Deviation

Table A.4. OM (%) for blueberry leaf extract treatments.

Extract	Green		Green		Green	
Time (wk)	1 1/2		3		6	
	Loose	Aggregate	Loose	Aggregate	Loose	Aggregate
Depth(cm)						
0-3	3.52±0.10	1.51±2.14	3.83±0.15	4.27±0.42		4.24±0.20
3-6	3.45±0.05	3.09±0.09	3.67±0.06	3.77±0.15	2.25±1.95	3.63±0.23
6-9	3.26±0.04	3.10±0.07	3.67±0.06	3.67±0.21	3.37±0.11	3.62±0.13
9-12	3.15±0.10	3.20±0.05	3.60±0.20	3.73±0.21	3.26±0.08	3.54±0.07
12-15	3.18±0.14	2.16±1.87	3.63±0.21	3.67±0.15	3.23±0.04	3.39±0.04

Table A.5. OM (%) for blueberry leaf extract treatments.

Extract	Brown				Mixed					
Time (wk)	1 1/2	3	6		9		12		21	
	Loose	Loose	Loose	Aggregate	Loose	Aggregate	Loose	Aggregate	Loose	Aggregate
Depth(cm)										
0-3	2.63±0.13	4.82±0.17	5.05±0.10	5.39±0.26	2.82±0.12	5.68±0.75	3.70±0.17	4.78±0.10	3.45±0.56	4.11±0.18
3-6	2.85±0.26	5.16±0.52	5.33±0.17	5.56±0.40	2.71±0.08		3.43±0.35	3.66±0.16	3.63±0.06	4.06±0.23
6-9	3.19±0.06	6.36±0.62	6.19±0.17	5.91±0.10	2.82±0.11		3.67±0.21	3.85±0.26	3.77±0.13	4.08±0.26
9-12	3.22±0.17	5.50±0.46	5.73±0.36	5.50±0.30	2.80±0.08		4.00±0.26	3.74±0.12	3.72±0.11	3.94±0.16
12-15							4.13±0.15	3.81±2.20	3.74±0.11	3.77±0.21
15-18							3.67±0.15	3.63±0.21	3.89±0.27	3.86±0.27
18-21							3.90±0.20	3.73±0.11	3.96±0.30	4.01±0.18
21-24							3.77±0.35	3.46±0.14	3.68±0.11	3.88±0.10
24-27							3.93±0.25	3.63±0.28	3.82±0.22	3.65±0.12
27-30							3.90±0.53	3.66±0.12	3.74±0.32	3.66±0.22

± Standard Deviation

Table A.6. OM (%) for 12-week treatments.

Extract	Pine		Fescue		Bent Grass	Bracken Fern
	Loose	Aggregate	Loose	Aggregate	Loose	Loose
Depth(cm)						
0-3	3.38±0.16	3.67±0.38	3.46±0.22	3.77±0.31	2.65±0.41	2.90±0.25
3-6	3.31±0.20	3.52±0.01	4.02±0.16	3.88±0.25	2.79±0.25	2.77±0.13
6-9	3.45±0.23	3.64±0.06	4.15±0.51	3.86±0.22	2.93±0.16	2.75±0.19
9-12	3.47±0.20	3.59±0.38	3.57±0.18	3.53±0.12	2.99±0.20	2.76±0.15
12-15	3.50±0.26	3.50±0.28	3.80±0.10	3.66±0.02	2.91±0.09	2.64±0.01
15-18	3.57±0.28	3.28±0.11	3.65±0.30	3.53±0.00	2.90±0.13	2.63±0.03
18-21	3.87±0.21	2.17±3.06	3.85±0.40	3.56±0.02	2.82±0.11	2.79±0.23
21-24	3.53±0.20	1.67±2.36	3.77±0.30	3.63±0.07	2.87±0.31	2.78±0.22
24-27	3.73±0.50	3.25±0.22	3.73±0.21	3.38±0.23	2.94±0.12	2.63±0.09
27-30	3.53±0.35	3.47±0.43	4.22±0.26	3.35±0.12	2.94±0.10	2.76±0.11

Table A.7. Al (%) for Blueberry leaf extract treatments.

Leaf Color	Brown							
Time (wk)	1 1/2	3		6	21		12, Ap	
Depth (cm)	Loose	Loose	Aggregate	Loose	Loose	Aggregate	Loose	Aggregate
0-3	0.30±0.01	0.20±0.03	0.20±0.03	0.20±0.01	0.38±0.05	0.37±0.09	0.35±0.04	0.35±0.03
3-6	0.29±0.02	0.28±0.08	0.28±0.05	0.24±0.00	0.37±0.05	0.44±0.06	0.35±0.09	0.39±0.03
6-9	0.29±0.03	0.39±0.04	0.39±0.03	0.42±0.02	0.34±0.02	0.40±0.04	0.36±0.08	0.41±0.03
9-12	0.28±0.02	0.38±0.05	0.35±0.01	0.42±0.05	0.34±0.02	0.42±0.06	0.44±0.13	0.39±0.04
12-15					0.36±0.01	0.39±0.04	0.41±0.07	0.40±0.03
15-18					0.38±0.03	0.45±0.02	0.40±0.02	0.39±0.02
18-21					0.40±0.03	0.44±0.08	0.38±0.05	0.41±0.01
21-24					0.42±0.02	0.41±0.05	0.39±0.06	0.38±0.04
24-27					0.37±0.05	0.38±0.03	0.38±0.07	0.37±0.02
27-30					0.41±0.04	0.39±0.03	0.38±0.04	0.35±0.04

Table A.8. Al (%) for Blueberry leaf extract treatments.

Leaf Color	Green					
Time (wk)	1 1/2		3		6	
Depth (cm)	Loose	Aggregate	Loose	Aggregate	Loose	Aggregate
0-3	0.24±0.02	0.27±0.06		0.30±0.01		0.31±0.00
3-6	0.25±0.04	0.31±0.03	0.30±0.02	0.34±0.01	0.29±0.04	0.33±0.03
6-9	0.24±0.05	0.30±0.03	0.32±0.01	0.31±0.01	0.31±0.00	0.33±0.03
9-12	0.24±0.03	0.28±0.04	0.30±0.02	0.32±0.01	0.31±0.01	0.32±0.02
12-15	0.24±0.02	0.29±0.02	0.29±0.02	0.33±0.02	0.30±0.03	0.33±0.02

Table A.9. Concentration of Al(%) following 12-week treatments.

Depth (cm)	Blueberry loose	Blueberry aggregate	Pine loose	Pine aggregate	Fescue loose	Bent Grass	Fern	Water
0-3	0.34±0.04	0.29±0.05	0.38±0.03	0.33±0.03	0.41±0.10	0.23±0.01	0.26±0.03	0.29±0.02
3-6	0.35±0.06	0.38±0.03	0.42±0.05	0.42±0.08	0.39±0.05	0.25±0.01	0.25±0.03	0.34±0.03
6-9	0.35±0.05	0.46	0.35±0.04	0.41±0.03	0.46±0.08	0.24±0.01	0.26±0.05	0.36±0.07
9-12	0.39±0.06	0.39±0.02	0.43±0.03	0.27±0.24	0.38±0.09	0.26±0.02	0.24±0.03	0.37±0.08
12-15	0.38±0.04	0.43	0.42±0.03	0.42±0.02	0.48±0.04	0.24±0.01	0.28±0.05	0.33±0.07
15-18	0.38±0.02	0.38±0.05	0.44±0.07	0.27±0.24	0.42±0.06	0.29	0.28±0.06	0.32±0.07
18-21	0.38±0.06	0.47±0.04	0.29±0.25	0.39±0.03	0.43±0.07	0.27	0.27±0.04	0.35±0.04
21-24	0.38±0.08	0.44±0.06	0.41±0.04	0.26±0.22	0.48±0.10	0.28	0.27±0.04	0.37±0.02
24-27	0.39±0.04	0.40±0.06	0.39±0.06	0.24±0.21	0.42±0.02	0.28	0.26±0.04	0.32±0.02
27-30	0.36±0.07	0.43±0.05	0.24±0.22	0.13±0.22	0.50±0.04	0.26	0.15±0.13	0.31±0.03

*The initial Al levels for the blueberry, pine and fescue columns were 0.34% and for the bent grass and bracken fern it was 0.23% .

Table A.10. Changes in Al concentrations (%) following 12-week treatments.

Change in Al Concentration in crushed ortstein following 12 week treatments								
Depth (cm)	Water	Blueberry, loose	Blueberry, aggregate	Pine, loose	Pine aggregate	Fescue, loose	Bent Grass	Fern
0-3	-0.06±0.02	-0.01±0.04	-0.05±0.05	0.03±0.03	-0.01±0.03	0.05±0.10	0.01±0.01	0.02±0.03
3-6	-0.01±0.03	0.00±0.06	0.04±0.03	0.07±0.05	0.07±0.08	0.05±0.05	0.01±0.01	0.02±0.03
6-9	0.01±0.07	0.01±0.05	0.12	0.01±0.04	0.07±0.03	0.12±0.08	0.00±0.01	0.02±0.05
9-12	0.02±0.08	0.04±0.06	0.042±0.02	0.09±0.03	0.07±0.24	0.04±0.09	0.02±0.02	0.00±0.03
12-15	-0.02±0.07	0.04±0.04	0.09	0.07±0.03	0.07±0.02	0.13±0.04	0.00±0.01	0.04±0.05
15-18	-0.02±0.07	0.04±0.02	0.02±0.05	0.10±0.07	0.07±0.24	0.07±0.06	0.05	0.04±0.06
18-21	0.00±0.04	0.04±0.06	0.13±0.04	0.08±0.25	0.05±0.03	0.09±0.07	0.03	0.03±0.04
21-24	0.02±0.02	0.04±0.08	0.10±0.06	0.07±0.04	0.04±0.22	0.14±0.10	0.04	0.04±0.04
24-27	-0.02±0.02	0.05±0.04	0.06±0.06	0.04±0.06	0.01±0.21	0.07±0.02	0.04	0.02±0.04
27-30	-0.04±0.03	0.02±0.07	0.08±0.05	0.02±0.22	0.03±0.22	0.15±0.04	0.02	-0.01±0.13
st. dev.	2.6	1.8	5.4	3.1	2.9	4.2	2.0	1.6

Table A.11. pH for leaf extract.

Extract	pH
Blueberry	4.40±1.27
Pine	4.50
Fescue	5.13±0.21
Bracken fern	5.52±0.11
Bent Grass	6.08±0.24

Table A.12. pH for blueberry leaf extract treatments.

Color	Green					
Time (wk)	1 1/2		3		6	
Depth (cm)	Loose	Aggregate	Loose	Aggregate	Loose	Aggregate
0-3	4.71±0.01	4.72±0.03	4.80±0.05	4.96±0.04		5.06±0.17
3-6	4.69±0.06	4.77±0.02	4.77±0.03	4.92±0.03	4.98±0.12	5.17±0.03
6-9	4.66±0.04	4.72±0.05	4.70±0.07	4.83±0.03	5.01±0.05	5.17±0.03
9-12	4.59±0.09	4.67±0.09	4.66±0.09	4.78±0.03	5.01±0.04	5.34±0.65
12-15	4.53±0.13	4.46±0.05	4.60±0.10	4.57±0.17	4.92±0.07	4.85±0.08

Table A.13. pH for blueberry leaf extract treatments.

Leaf Color	Brown					Mixed			Mixed, Ap	
Time (wk)	1 1/2		3	6		9	12		21	
Depth (cm)	Loose	Aggregate	Loose	Loose	Aggregate	Loose	Loose	Aggregate	Loose	Aggregate
0-3	4.87±0.04	5.39±0.09	4.85±0.02	5.15±0.11	5.56±0.13	5.42±0.05	5.44±0.06	5.94±0.21	5.63±0.05	6.43±0.23
3-6	4.71±0.05		4.69±0.06	4.88±0.05	5.00±0.05	5.06±0.03	5.26±0.06	5.42±0.04	5.55±0.18	5.50±0.15
6-9	4.68±0.03		4.58±0.03	4.68±0.02	5.13±0.64	4.79±0.04	5.05±0.19	5.25±0.31	5.32±0.08	5.25±0.07
9-12	4.63±0.01		4.54±0.03	4.62±0.04	4.45±0.04	4.73±0.01	5.02±0.15	5.16±0.20	5.25±0.06	5.19±0.01
12-15							4.93±0.13	4.98±0.03	5.24±0.12	5.27±0.16
15-18							4.88±0.10	4.92±0.12	5.18±0.13	5.26±0.11
18-21							4.88±0.13	5.03±0.07	5.13±0.09	5.17±0.14
21-24							4.78±0.11	4.83±0.19	5.16±0.12	5.03±0.08
24-27							4.73±0.09	4.83±0.23	5.19±0.06	5.10±0.11
27-30							4.86±0.09	4.95±0.24	5.14±0.03	4.93±0.16

Table A.14. pH for 12-week treatments.

Depth	Blueberry		Pine		Fescue		Bent grass	Bracken Fern	Water
	Loose	Aggregate	Loose	Aggregate	Loose	Aggregate	Loose	Loose	Loose
0-3	5.44±0.06	5.94±0.21	4.91±0.69	5.95±0.19	5.89±1.16	7.26±0.26	6.61±0.54	5.90±1.03	4.78±0.13
3-6	5.26±0.06	5.42±0.04	5.20±0.03	5.10±0.13	5.09±0.05	6.08±0.06	6.05±0.31	5.06±0.22	4.76±0.03
6-9	5.05±0.19	5.25±0.31	5.03±0.02	5.03±0.16	4.72±0.11	6.15±0.51	5.47±0.29	4.75±0.17	4.77±0.05
9-12	5.02±0.15	5.16±0.20	4.95±0.07	4.94±0.08	4.82±0.42	5.96±1.35	4.97±0.05	4.53±0.25	4.76±0.02
12-15	4.93±0.13	4.98±0.03	4.91±0.09	4.81±0.07	4.78±0.41	5.95±1.30	4.72±0.21	4.47±0.18	4.80±0.06
15-18	4.88±0.10	4.92±0.12	4.81±0.06	4.86±0.09	4.67±0.18	6.35±0.90	4.47±0.17	4.37±0.05	4.81±0.01
18-21	4.88±0.13	5.03±0.07	4.76±0.05	4.79±0.12	4.84±0.45	6.09±1.05	4.35±0.09	4.40±0.11	4.71±0.02
21-24	4.78±0.11	4.83±0.19	4.66±0.07	4.60±0.08	4.64±0.27	6.09±0.97	4.54±0.22	4.36±0.15	4.78±0.04
24-27	4.73±0.09	4.83±0.23	4.56±0.12	4.56±0.11	4.54±0.13	5.61±0.83	4.65±0.24	4.43±0.04	4.79±0.05
27-30	4.86±0.09	4.95±0.24	4.51±0.07	4.44*	4.36±0.12	4.54±0.31	4.79±0.24	4.33±0.07	4.69±0.07

n=1

Table A.15. Temperature (°C) of crushed ortstein columns after 12-week treatments.

	5 cm	15 cm	25 cm
Blueberry	21.4±0.06	21.6±0.06	21.5±0.06
Blueberry with Ap	21.4±0.00	21.6±0.00	21.6±0.06
Pine	21.2±0.06	21.5±0.06	21.4±0.15
Water	21.2±0.06	21.3±0.11	21.2±0.15
Fescue	20.9±0.10	21.2±0.00	21.1±0.06
Fescue with Ap	20.9±0.00	21.2±0.06	20.8±0.07
Bent grass & rhizosphere	21.6±0.06	21.7±0.06	21.5±0.00
Bent grass, rhizosphere and blueberry extract	21.6±0.10	21.6±0.10	20.7±0.42
Fescue & rhizosphere	21.2±0.06	21.2±0.12	20.4±0.55
Fescue, rhizosphere and blueberry extract	21.5±0.06	21.6±0.06	20.9±0.47
Bent grass	21.1±0.17	21.2±0.10	20.8±0.10
Bracken fern	21.3±0.15	21.5±0.06	21.3±0.15

Table A.16. Temperature (°C) Blueberry leaf extract treatments

Leaf Color	Green		Brown			Mixed		
Time (wk)	1 1/2	6	1 1/2	3	6	9	12	21
Depth (cm)								
5	22.6±0.14	22.4±0.06	21.9±0.06	20.8±0.06	20.8±0.00	22.6±0.06	21.4±0.06	21.8
10	22.4±0.14	22.4±0.06	21.4±0.15	19.9±0.00	20.4±0.06	22.0±0.10		
15							21.6±0.06	22.0
25							21.5±0.06	21.9

Table A.17. Weight change and strength for ortstein pieces after 12-week treatments.

Treatment	Extract		% Wt. change	Strength (g)
	Blueberry	Blueberry	215.3±183.4	1007±415
Ap	Blueberry	Blueberry	288.3±173.3	1072±713
	Fescue	Fescue	118.1±106.6	742±398
Ap	Fescue	Fescue	80.1±45.6	737±439
	Bent grass	Bent grass	2.5±43.4	1453±744
	Bracken Fern	Bracken Fern	11.2±3.73	1107±481
Rhizosphere	Fescue	Fescue	-7.5±11.0	1211±1007
Rhizosphere	Blueberry	Fescue	6.9±20.8	1856±757
Rhizosphere	Bent grass	Bent grass	18.2±51.2	1190±549
Rhizosphere	Blueberry	Bent grass	9.2±31.6	1215±551
	Water	Water	-8.3±5.8	649±661
Symbex	Water	Symbex	-10.0±7.4	760±407
Symbex (x10)	Water	Symbex (x10)	-1.5±6.0	611±698
Symbex (x100)	Water	Symbex (x100)	27.1±32.7	604±339
Symbex	Blueberry	Symbex	2.1±17.4	995±540
	Pine	Pine	16.1±25.1	1270±710

n=15

Appendix B

Organic Acid Study Data Tables

Table B.1. Aggregation of crushed ortstein treated with organic acids, water and Super Symbex 4X after 5-week treatment.

	Loose (g)	Aggregate (g)	Ratio	% Aggregation
Water	5.01±0.06	0.07±0.05	68.32±114.43	1.4
Water & Symbex	3.48±0.32	1.19±0.22	2.93±0.74	25.5
PCA	1.79±0.75	2.87±1.03	0.62±0.67	61.6
PCA & Symbex	3.16±0.40	1.24±0.62	2.54±2.04	28.2
VA	2.93±0.70	2.02±0.68	1.45±1.13	40.8
VA & Symbex	2.99±0.33	1.54±0.34	1.94±0.73	34.0
ρHBA	2.63±1.33	2.25±1.38	1.17±2.49	46.1
ρHBA & Symbex	3.12±0.26	1.40±0.24	2.24±0.58	30.9
Cat	4.48±0.21	0.50±0.21	9.02±5.19	10.0
Cat & Symbex	3.59±0.38	0.59±0.40	6.08±4.35	14.1

*PCA, Protocatechuic Acid
VA, Vanillic Acid
ρHBA, para-hydrobenzoic Acid
Cat, Catechol

Table B.2. OM (%) for crushed ortstein treated with organic acids, with and without Super Symbex 4X after 5-week treatment. (Composite samples)

	Loose		Aggregate	
	Without Symbex	With Symbex	Without Symbex	With Symbex
Water	3.73	3.77	4.01	3.72
PCA	2.91	3.35	3.78	2.44
VA	3.54	4.04	3.54	3.32
ρHBA	3.37	3.65	4.58	3.35
Cat	3.51	3.78	8.93	4.61

Table B.3. pH of loose crushed ortstein treated with organic acids, with and without Super Symbex 4X after 5-week treatment. (Composite samples)

	Without Symbex	With Symbex
Water	4.56	5.28
PCA	4.53	5.35
VA	4.57	5.30
ρHBA		5.39
Cat	4.56	4.53

Appendix C

Pit Study Data Tables

Table C.1. OM (%) values for pit samples.

	Control	Jack Pine	Red Pine
A	6.45±0.21		
E	1.80±1.13	0.73±0.06	0.83±0.12
Bs1	1.25±0.21	0.70±0.10	0.53±0.15
Bs2	0.80		
BC	0.55±0.07		
C	0.30±0.00	0.23±0.12	0.23±0.06

Table C.2. Al (%) values for pit samples.

Ammonium Oxalate Extraction			
	Control	Jack Pine	Red Pine
A	0.041±0.02		
E	0.039±0.04	0.009±0.01	0.007±0.00
Bs1	0.154±0.12	0.041±0.05	0.016±0.01
Bs2	0. 182		
BC	0. 109		
C	0.026±0.08	0.004±0.00	0.004±0.00

Table C.3. Fe (%) values for pit samples.

Ammonium Oxalate Extraction			
	Control	Jack Pine	Red Pine
A	0.088±0.02		
E	0.068±0.05	0.035±0.01	0.039±0.01
Bs1	0.215±0.10	0.045±0.02	0.025±0.01
Bs2	0.220		
BC	0.129±0.11		
C	0.032±0.01	0.022±0.01	0.023±0.002

Table C.4. pH values for pit samples.

	Control	Jack Pine	Red Pine
A	4.57±0.16		
E	4.43±0.02	5.22±0.40	4.84±0.13
Bs1	4.94±0.23	6.37±0.95	5.58±1.01
Bs2	5.41		
BC	5.26		
C	5.57±0.06	7.16±0.89	6.34±0.55

Appendix D

High Pressure Liquid Chromatography Figures

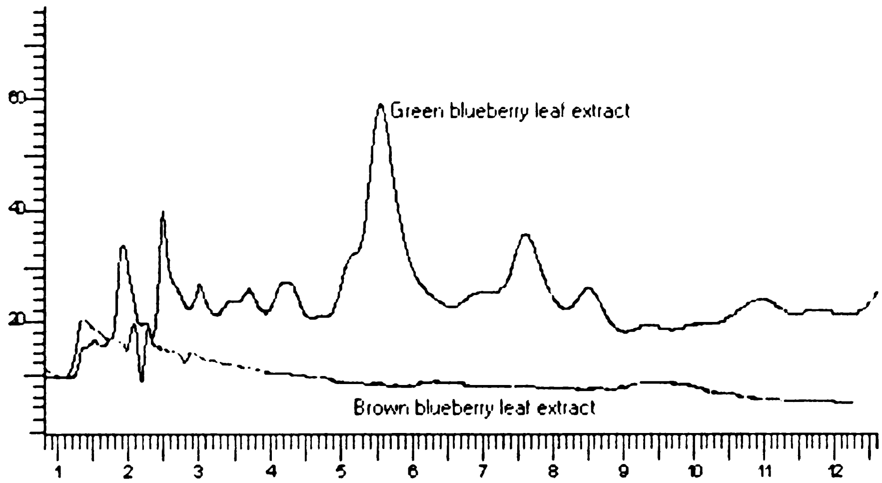


Figure 1a. HPLC chromatograph of green and brown blueberry leaf extract.

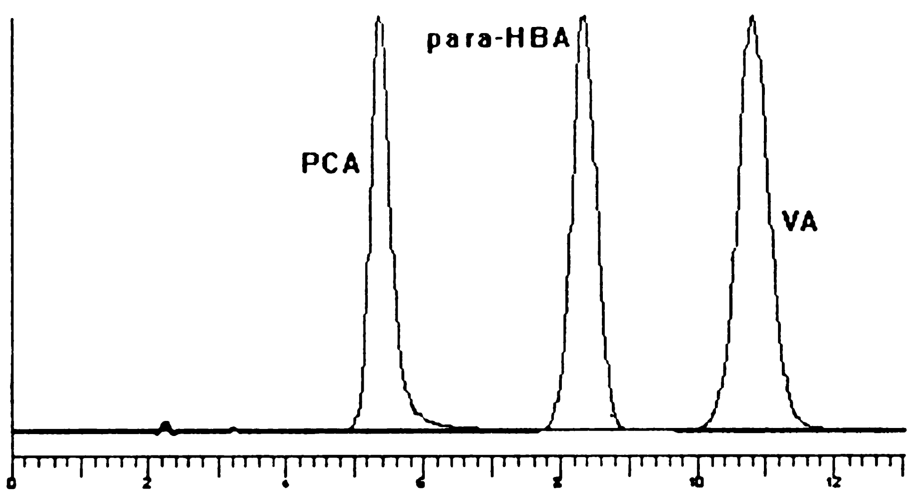


Figure 1b. HPLC chromatograph of standards: protocatechuic acid (PCA), para-hydrobenzoic acid (para-HBA) and vanillic acid (VA).

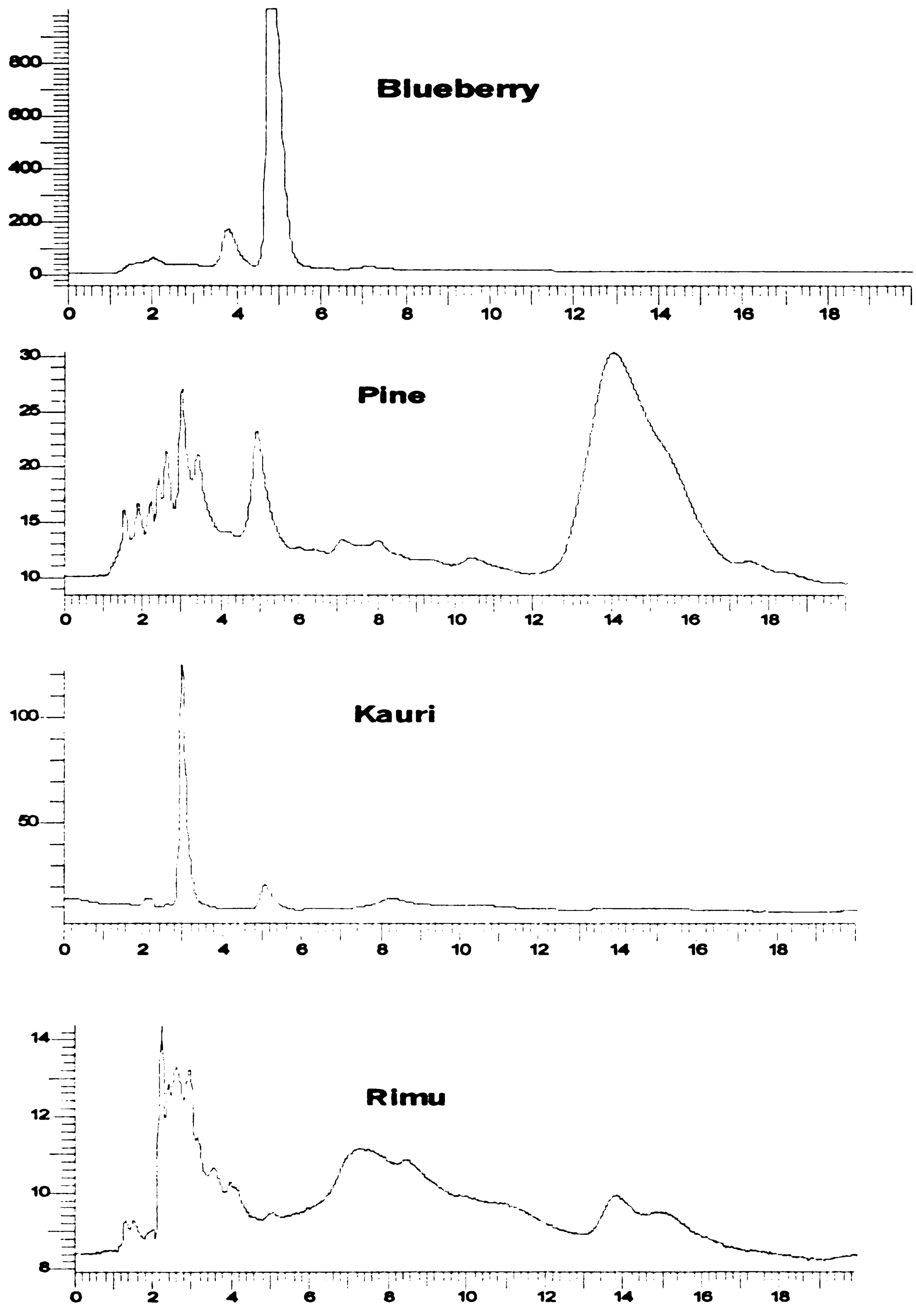
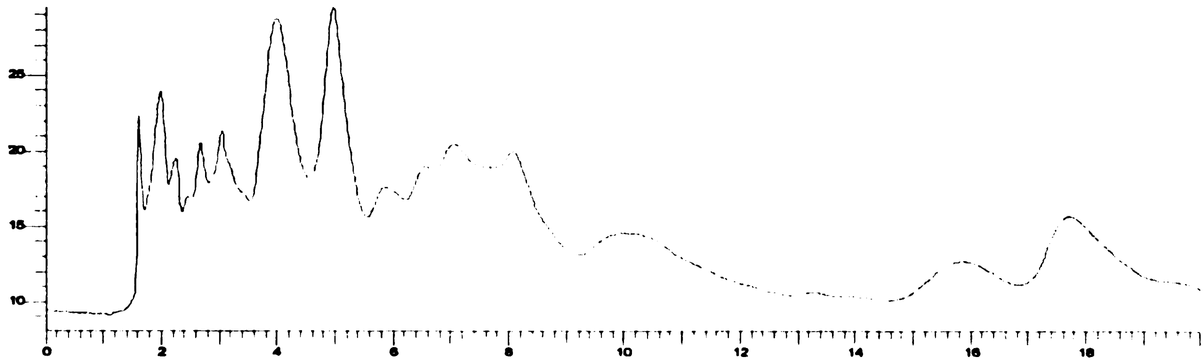
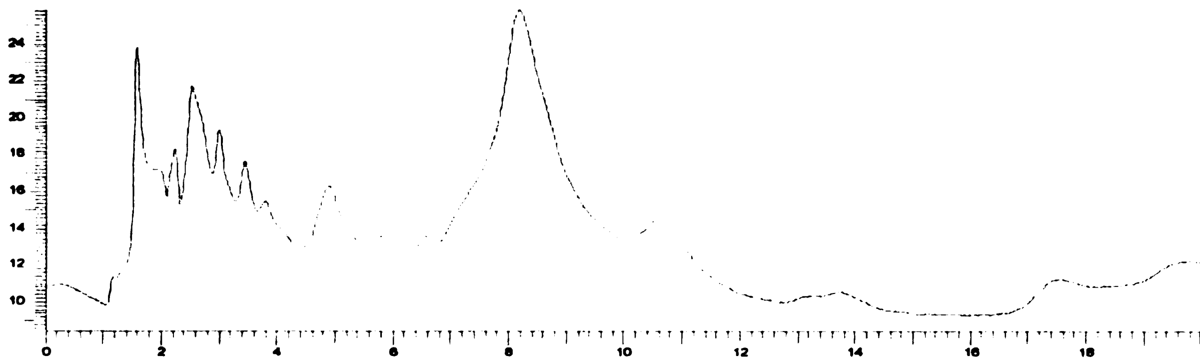


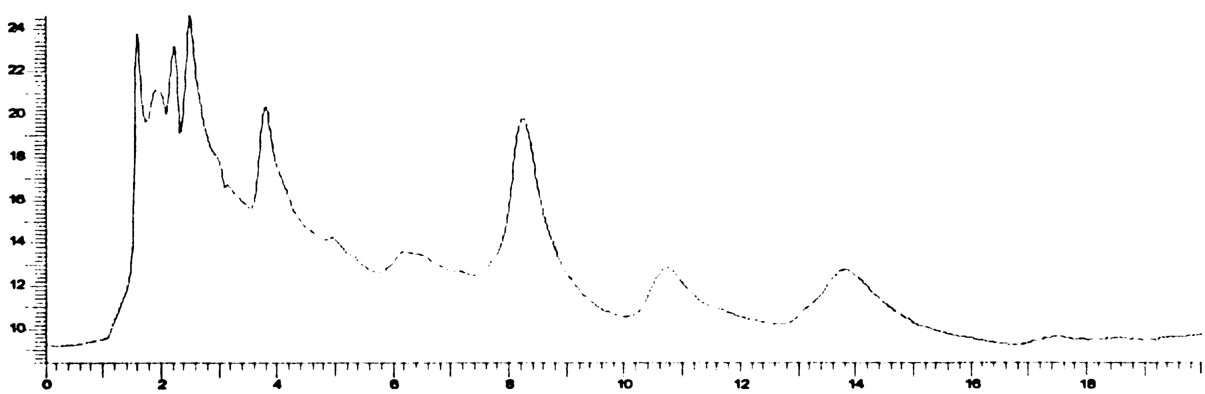
Figure D.2 HPLC chromatographs of podzolizer leaf extract.



a. Bracken Fern



b. Fescue



c. Bent grass

Figure D.3 HPLC chromatographs of depodzolizer leaf extract.

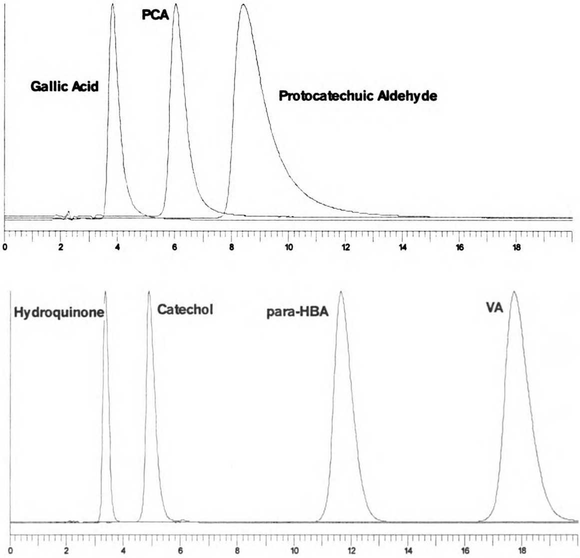


Figure D.3 HPLC chromatographs for organic compound standards.