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SULFATE ADSORPTION IN MICHIGAN FOREST SOILS

by

Neil William MacDonald

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

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ABSTRACT

SULFATE ADSORPTION IN MICHIGAN FOREST SOILS

by

Neil William MacDonald

The occurrence of acidic atmospheric deposition raised concerns over adverse cation leaching effects on Michigan forest soils with low cation exchange capacities. Leaching effects of acid deposition depend on mobility of sulfate in the soil. Little was known, however, concerning the ability of these soils to adsorb sulfate. The objectives of this study were to determine the ability of representative Michigan forest soils to adsorb sulfate, to relate sulfate adsorption to soil properties, and to develop equations to predict sulfate adsorption in similar forest soils.

Frigid zone soil series studied were Grayling (Typic Udipsamments), Rubicon (Entic Haplorthods), Kalkaska (Typic Haplorthods), and Montcalm (Eutric Glossoboralfs). Mesic zone series studied were Spinks (Psammentic Hapludalfs) and Oshtemo (Typic Hapludalfs). Six randomly located pedons of each series were sampled. Sulfate adsorption was determined by shaking 10 gram soil samples for 24 hours in 50 mL 0.01 M $CaCl_2$ solution containing 10 mg SO_4-S L^{-1}. Solution filtrates were turbidimetrically analyzed for SO_4-S and adsorption was calculated from reduction in SO_4-S concentration.

Bw, Bs, and Bh horizons of frigid zone soils and E and

Bt horizons of mesic zone soils had the highest sulfate adsorbing abilities. No significant differences were found between series in total sulfate adsorptive capacity. Differences between series in location of adsorption within the soil profile suggested that the flow path of percolating solutions may be more important in determining sensitivity to acid deposition effects than total adsorptive capacities.

In subsurface soil horizons, sulfate adsorption was most strongly correlated with dithionite-citrate and ammonium oxalate extractable Al. Multiple regression analyses demonstrated that sulfate adsorption in the soils studied could be predicted using relatively few variables derived from commonly measured soil properties. Maximum coefficients of multiple determination (R^2) ranged from 0.85 to 0.94, depending on grouping of soils and specific predictors employed.

Quantities of sulfate adsorbed indicated that Michigan forest soils are relatively weak sulfate adsorbers. Calculations based on total adsorptive capacities and present levels of sulfate deposition suggested that sulfate retention by these soils will reduce, but not prevent, cation losses resulting from acid deposition for time periods measured in years or decades.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Chapter I

INTRODUCTION

The phenomenon of "acid rain" has received major attention only during the last fifteen years, but in reality acid deposition has developed largely unnoticed since the advent of industrialization (Cowling, 1982). In North America, the greatest increase in precipitation acidity occurred during the last forty years, most noticeably in the northeastern United States and eastern Canada (Bormann, 1974; Cogbill and Likens, 1974). The recent decrease in precipitation pH is primarily the result of combustion of fossil fuels and the consequent emission of acid-forming sulfur and nitrogen oxides (Galloway et al., 1976; Likens et al., 1979). In contrast to the estimated pre-industrial pH range from 5 to 8, precipitation in the northeastern United States averaged around pH 4 in the 1970's (Bormann, 1974; Likens and Bormann, 1974; Norton, 1977), with similar low pH values currently recorded (NADP, 1985a; 1985b; 1986). Precipitation pH in Michigan presently ranges from 3.5 upwards to 7.5, the pH of most precipitation events falling close to a value of 4.5 (MacDonald, 1983; NADP, 1985b; 1986). While not as acidic as rains in the northeastern states, the pH of rain in Michigan is substantially lower than that expected for unpolluted rainfall. Annual sulfate deposition in the lower peninsula of Michigan ranges from

0.6 to 0.9 g S m^{-2}, between the > 1.0 g S m^{-2} in the most heavily impacted eastern states and the < 0.3 g S m^{-2} in the lightly impacted western states (NADP, 1985a; 1985b; 1986).

Acid deposition is a complex problem with major ecological, political, and international consequences (Cowling and Linthurst, 1981; Cowling, 1982). Chronic acidic precipitation in the northeastern United States, Canada, and Europe raised concerns over possible regional impacts on terrestrial and aquatic ecosystems distant from the sources of pollution (Dochinger and Seliga, 1976; Hutchinson and Havas, 1980; Drablos and Tollan, 1980). Widespread decline in European forests related to atmospheric pollution and similar but unexplained forest declines in the eastern United States intensified concern in recent years (Schutt and Cowling, 1985; Hinrichsen, 1986; Woodman and Cowling, 1987). The role of acid deposition in forest decline has been difficult to quantify because acid deposition produces stress in addition to those occurring naturally (Woodman and Cowling, 1987). Decisions to implement pollution control measures are contingent upon 1) scientific evidence relating acid deposition to forest decline; 2) ecologic and economic consequences of unabated acid deposition; 3) regional sources of pollutants; 4) location and extent of sensitive ecosystems receiving acid deposition; and 5) the capacity of these sensitive ecosystems to buffer adverse acid deposition effects. An intimate relationship exists between soils and the forest

ecosystems they support; an understanding of the interactions between soils and acid deposition is therefore necessary to define and predict effects on sensitive ecosystems (Fernandez, 1985).

A preliminary classification of Michigan soils, based on criteria developed by McFee (1980), indicated that over seventy soil series covering an estimated forty percent of the land area of Michigan were potentially susceptible to adverse effects from acid deposition (Appendix A). These included the major forest soils of Michigan. Impingement of chronically acidic precipitation on these soils is cause for concern because of potential negative impacts on the productivity and ecological integrity of the forests they support. Adverse effects could result from cation removal and aluminum mobilization in soils. Leaching of basic cations may cause impoverishment of soils with time, while mobilization of aluminum may cause biological toxicities, both within the terrestrial ecosystem and in adjoining aquatic ecosystems (Reuss, 1983). Increased knowledge of the sensitivity of Michigan's forest soils to atmospheric acid inputs is needed to predict the impacts of acid deposition and to determine management practices required to ameliorate any resulting adverse soil conditions.

CLASSIFICATION OF SOIL SENSITIVITY

Klopatek et al. (1980) rated sensitivity of soils in the eastern United States using average values of pH, cation

exchange capacity, and base saturation in the upper 20-25 cm of typic great soil groups to characterize soil sensitivity of county-sized mapping units. Because of its development for regional classification and neglect of soils low in cation exchange capacity, base saturation, and pH, the results of this study could not be readily applied to Michigan's forest soils on a series level.

Cowell et al. (1980) suggested sensitivity criteria for predicting impacts of acid deposition on forest productivity based on sulfate adsorption capacity, exchangeable bases, and soil depth. Potential for exchangeable base loss was considered a better measure of sensitivity than cation exchange capacity alone. Sulfate adsorption capacity was seen as important in determining potential for leaching loss, while soil depth was important from the aspect of nutrient cycling and uptake by root systems. Lack of information on sulfate adsorption ability prevented application of these sensitivity criteria to Michigan's forest soils.

McFee (1980) estimated sensitivity of soils in the eastern United States to acid precipitation based largely on cation exchange capacity in the top 25 cm of soil. If an acid input of 100 cm of pH 3.7 rain per year equalled 10-25% of the cation exchange capacity, soils were rated as slightly sensitive. If this input exceeded 25% of the cation exchange capacity, the soils were considered sensitive. Soils with cation exchange capacity greater than

15.4 cmol (+) kg^{-1} were rated as non-sensitive. While these criteria were limited, they did allow tentative estimates of soil sensitivity on a soil series level for Michigan soils (Appendix A).

The major factor affecting soil sensitivity which required further research was the ability of Michigan forest soils to retain sulfate. Atmospheric deposition of H^+ and SO_4^{2-} has the potential to reduce soil fertility through accelerated leaching of basic cations, but adsorption or retention of sulfate by the soil can counteract this effect. The focus of this study is sulfate adsorption in Michigan forest soils, and the relationship of this factor to acid deposition effects. The soils of concern are those Michigan forest soils believed to be sensitive to adverse effects from acid deposition because of their physico-chemical properties. The initial sensitivity classification suggests these soils are well- to moderately well-drained, coarse-textured Entisols, Alfisols, and Spodosols (Appendix A).

A conceptual framework within which to stratify sampling of these soils is presented in Figure 1.1. Three major taxonomic groups are Typic Udipsamments, Typic Hapludalfs, and Typic Haplorthods. Intergrades transitional between typic subgroups are located along the axes. Selected Michigan soil series representative of taxonomic subgroups and potentially sensitive to acid deposition are indicated. Soils within each subgroup should have similar abilities to adsorb sulfate, while adsorptive ability may

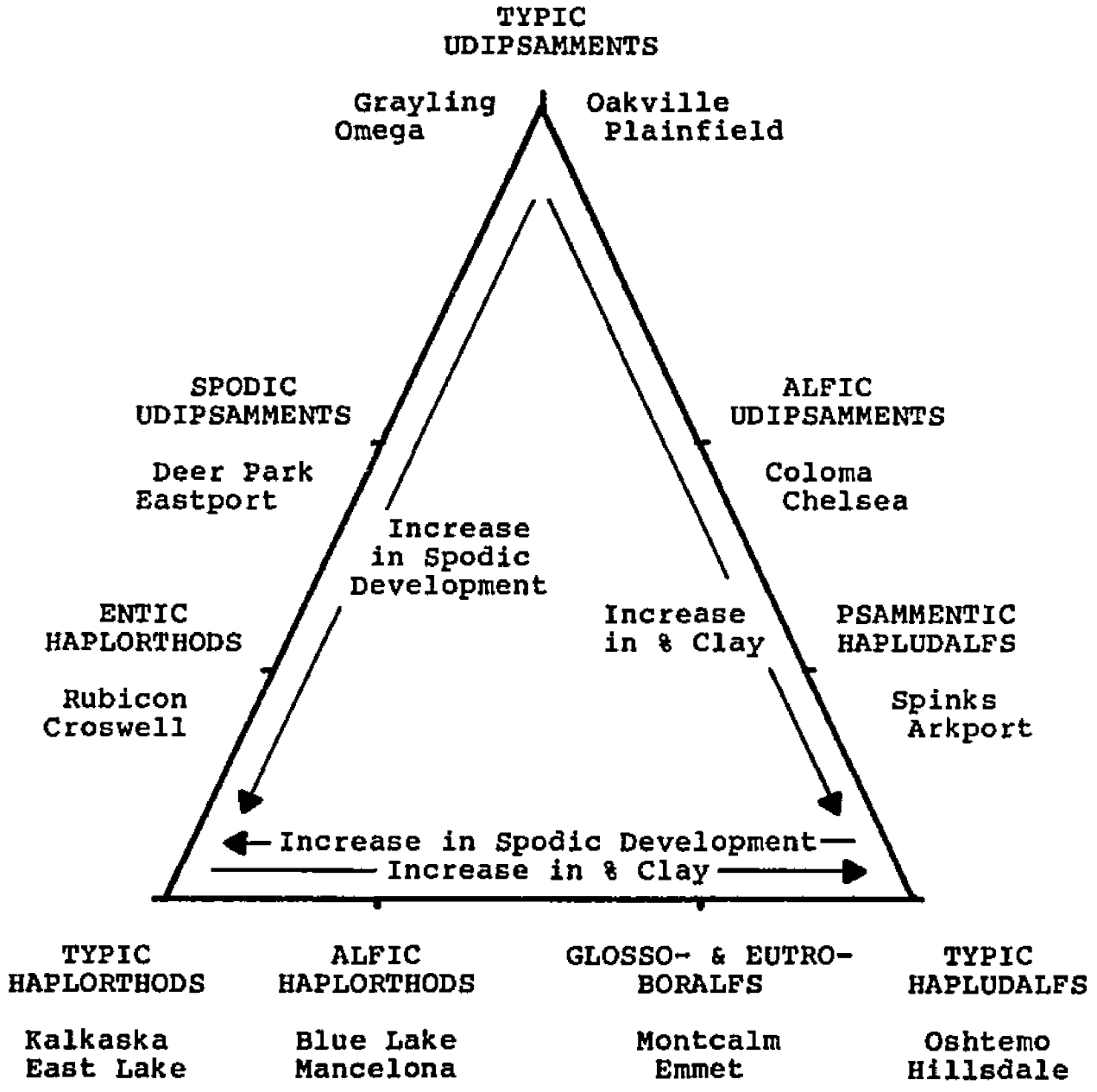

Figure 1.1

Representative Michigan Soil Series Potentially Sensitive to Acid Deposition in Relation to Soil Taxonomy

differ between subgroups because of differences in soil properties. In making an assessment of sulfate adsorption abilities of Michigan forest soils, these three gradients of soil profile development provide a basis to project experimental results to a variety of forest soils.

OBJECTIVES

The first objective of this study was to determine the ability of representative Michigan forest soils to adsorb sulfate under laboratory conditions and to determine initial levels of extractable sulfate present. The second objective was to relate sulfate adsorption to other soil properties commonly used for soil classification. A final objective was to develop regression equations and to use existing soil characterization data to predict sulfate adsorption in similar Michigan forest soils.

Chapter II

LITERATURE REVIEW: ADSORPTION AND RETENTION OF SULFATE BY SOILS

Sulfate mobility in the soil is an important factor affecting forest soil sensitivity to cation leaching effects of acid precipitation. Atmospheric inputs of H_2SO_4 provide a major source of both H^+ ions for cation replacement and SO_4^{2-} anions for cation transport in forest soils affected by acid precipitation (Cronan et al., 1978; Cronan and Schofield, 1979; Mollitor and Berg, 1980). Since the sulfate associated with acid inputs must be mobile in the soil if leaching of bases is to occur, adsorption or retention of sulfate by the soil can reduce or prevent cation leaching (Johnson et al., 1982). If sulfate loading exceeds the capacity of the soil to retain sulfate, leaching losses will occur when soil adsorption sites are filled (Reuss, 1977; Johnson, 1980; Morrison, 1981).

This review examines physico-chemical factors and soil properties related to sulfate adsorption and briefly discusses postulated sulfate retention mechanisms. The primary intent of the literature review was to provide a foundation for subsequent study of sulfate adsorption in Michigan forest soils. Application to the present study is discussed on page 21. Literature pertinent to results of the present study is also cited in Chapters III to VII.

FACTORS INFLUENCING SULFATE RETENTION IN SOILS

Sulfate retention by soils is influenced by a variety of soil chemical properties. Sulfate adsorption by soils or soil constituents is highly pH dependent, with adsorption increasing as pH decreases (Kamprath et al., 1956; Parfitt, 1982). The effect of pH on sulfate adsorption is greater in soils containing higher amounts of sesquioxides, exchangeable aluminum, or amorphous materials such as allophane (Chao et al., 1963). Sulfate adsorption by soils increases with increasing concentration of sulfate in solution (Kamprath et al., 1956; Chao et al., 1962a; Rajan, 1978; Rajan, 1979a; Couto et al., 1979).

Length of contact between soil and solution affects sulfate retention. Barrow and Shaw (1977), working with an Australian soil developed in laterite residuum, found that after two days of contact 97% of added sulfate could be desorbed, but after 105 days of contact only 64% could be desorbed. These results suggested that slow changes in the nature of the link between adsorbed sulfate and the soil occurred over time. While adsorption of sulfate from solution also increased with temperature of incubation, temperature effects were less marked for sulfate than for phosphate (Barrow and Shaw, 1977). Sulfate adsorption in the surface horizon of a sandy loam "Calcic Cambisol" was fully reversible after an equilibration period of a few hours, but not after periods of days (Sanders and Tinker, 1975). Sulfate incubated with soil prior to leaching was

much less prone to subsequent movement than sulfate added with the leaching solution (Bolan et al., 1986a).

The type of cation present in solution or on the exchange complex affects sulfate adsorption. Lichtenwalner et al. (1923) found that sulfate adsorption by Fe and Al hydroxides was least in K_2SO_4 solution, intermediate in $MgSO_4$ solution, and greatest in $CaSO_4$ solution. Chao et al. (1963) had similar results; the magnitude of sulfate adsorption from different salt solutions decreased in the order $CaSO_4 > K_2SO_4 > (NH_4)_2SO_4 > Na_2SO_4$. The magnitude of sulfate adsorption by soils saturated with different cations also followed the order of chemical valency of the saturating cations, with $Al^{3+} > Ca^{2+} > K^+ > Na^+$. The cation effect was in addition to the pH effect over the pH range of 4 to 7. Aluminum saturation increased sulfate retention over that of the original soil, while saturation with calcium, potassium, or sodium decreased adsorption below that of the original soil (Chao et al., 1963). Sulfate adsorption in the surface horizons of two New Zealand soils decreased with increasing ionic strength of the supporting NaCl solution. Adsorption was least in 1.0 M NaCl, intermediate in 0.1 M NaCl, and greatest in 0.01 M NaCl. This relationship was consistent over a solution pH range from 3.0 to 8.0 (Bolan et al., 1986b). Johnson et al. (1986) noted that their previous anion adsorption studies using Na^+ salts gave extremely variable results. Subsequent S-adsorption studies using Ca^{2+} salts were less variable and

provided greater differentiation among soils.

There are marked differences in the effects of other anions upon sulfate retention by soils. The presence of phosphate, molybdate, or fluoride in solution strongly reduced sulfate adsorption (Ensminger, 1954; Kamprath et al., 1956; Chao, 1964; Parfitt, 1982). Depression of sulfate adsorption was proportional to the concentration of the interfering anion. Metson and Blakemore (1978) reported the competitive effects of phosphate on sulfate adsorption were greatest in soils with weakly developed anion-retention properties. Soils with higher levels of anion retention had the capacity to retain added sulfate even in the presence of a similar concentration of phosphate. Nitrate, chloride, silicate, and acetate anions did not reduce sulfate adsorption in the pH range of 4 to 6 (Chao, 1964). Similarly, addition of KCl and KNO_3 solutions to a podzolic brown earth soil did not impair adsorption of sulfate from the percolating solution (Khanna and Beese, 1978).

Soil mineralogic factors have a major effect on sulfate adsorption. Sulfate retention by clays was highest in kaolinite, intermediate in illite, and least in bentonite. Aluminum saturated clays retained more sulfate than hydrogen saturated clays (Chao et al., 1962b). A loam soil high in allophane adsorbed almost five times more SO_4-S than a silt loam which had mineralogy dominated by vermiculite (Bolan et al., 1986a). Chao et al. (1962a) reported that the major distinguishing characteristics of sulfate retentive soils

were their high levels of free Al and Fe oxides and exchangeable aluminum. In the acid range, the amount of sulfate adsorbed by soils was proportional to the amounts of hydrous Fe and Al oxides present (Chao et al., 1964).

Barrow et al. (1969) related the sulfate adsorption ability of a variety of Australian soils to pedogenic factors. In most soils, the ability to adsorb sulfate increased with average annual rainfall. The correlation with rainfall was explained as a reflection of reactive aluminum contents and soil pH, properties related to the amount of rainfall. Soils derived from basalt had a higher sulfate adsorbing ability than soils derived from granitic or sedimentary rocks, possibly because soils derived from siliceous parent materials had less aluminum than soils derived from basalt. The occurrence of sulfate adsorbing soils was favored by low temperature, a factor associated with soil pH differences.

Metson and Blakemore (1978), working with a variety of New Zealand soils, found that soils with low levels of native adsorbed sulfate (phosphate extractable S) had very little capacity to retain added sulfate. Higher levels of native adsorbed sulfate indicated soils with capacities to adsorb additional sulfate.

Ensminger (1954) found that subsurface soil layers usually contained more sulfate and were capable of retaining more sulfate than the surface layers. Sulfate retention in A horizons of acid forest soils was observed to be very low,

but increased substantially in the B horizons (Singh, 1980b; Johnson and Todd, 1983; Fuller et al., 1985; Weaver et al., 1985). Young soils developed after the most recent glaciation generally have less sulfate adsorption capacity than soils developed over longer times (Abrahamsen, 1980).

Soil constituents related to sulfate retention differ in ability to adsorb sulfate. Ensminger (1954) found that iron minerals adsorbed small amounts of sulfate, kaolinite was intermediate in sulfate adsorption, while dehydrated Al_2O_3 adsorbed the most sulfate. Aylmore et al. (1967) found that sulfate adsorption by an aluminum oxide (pseudoboehmite) and an iron oxide (hematite) was almost completely irreversible with respect to equilibrium concentration, while adsorption by kaolinite clays was largely reversible. Aluminum oxides were more effective in retaining sulfate than iron oxides in a pure state (Aylmore et al., 1967), and when both were added as coatings on soil particles (Chao et al., 1964). When added to soil, the Fe system exhibited increasing adsorption with increasing acidity whereas the Al system showed a maximum at pH 4.0. Subsequent decreases in sulfate adsorption by Al-coated soils at pH values less than 4 were associated with dissolution of the hydrous Al-oxide and destruction of adsorption sites (Chao et al., 1964).

Extractable sesquioxide fractions and associated chemical properties of soils have been related to sulfate adsorption. In experiments with four Australian coastal

plain soils, Barrow (1967) found that dithionite-citrate extractable Fe was not correlated with sulfate adsorption, but dithionite-citrate extractable Al was positively correlated with sulfate adsorption. Total Kjeldahl N was negatively related to sulfate adsorption, possibly due to its relation to organic matter content. Sulfate adsorbed by surface horizons of eight West Indian soils was correlated ($r = 0.73$) with NaOH extractable Al_2O_3 (Haque and Walmsley, 1973). Correlations with pH, organic matter, clay, silt + clay, and dithionite-citrate Fe in the same soils were not significant, possibly because of the small number of samples studied.

Singh (1980b) found that dithionite-citrate Al ($r = 0.73$), dithionite-citrate Fe ($r = 0.62$), and phosphate-extractable SO_4^{2-} ($r = 0.77$) were correlated with SO_4^{2-} adsorption in Typic Udipsamment, Umbric Dystrochrept, and Aquic Haploboroll soils ($n = 17$). Soil pH, clay content, and organic C were not correlated with SO_4^{2-} adsorption in these soils. Removal of Al and Fe oxides resulted in a substantial reduction in S-adsorption in a Typic Udipsamment, but had less effect on S-adsorption in an Umbric Dystrochrept. This result was related to initially higher amorphous inorganic Al and Fe in the Udipsamment and higher clay content in the Dystrochrept (Singh, 1984b).

Three northeastern United States Spodosols were found to have major portions (16 to 64 mg S kg^{-1}) of native SO_4^{2-} present in water insoluble (phosphate extractable) form in

Bs1 and Bs2 horizons. Crystalline Fe (r = 0.42, n = 24 to r = 0.96, n = 10), dithionite-citrate Al (r = 0.87, n = 24), and ammonium oxalate Al (r = 0.73, n = 24) appeared to explain most of the variability in SO_4^{2-} adsorption capability. Correlations with dithionite-citrate, ammonium oxalate, and sodium pyrophosphate extractable Fe ranged from 0.50 to 0.53 (n = 24). Organic carbon, % clay, and H^+ were not correlated with SO_4^{2-} adsorption (Fuller et al., 1985).

Johnson and Todd (1983) observed that crystalline Fe (dithionite-citrate Fe minus ammonium-oxalate Fe) was the parameter most closely related (r = 0.69, n = 22) to total sulfate adsorbed in the B horizons of a variety of North American forest soils. A combination of percent carbon, dithionite-citrate and oxalate extractions for Fe and Al offered promise for predicting sulfate adsorption. Percent clay, pH, and pyrophosphate extractable Fe and Al were inconsistently related to sulfate adsorption. Both surface soils and B horizons of Spodosols had relatively poor sulfate adsorption properties, even when dithionite-citrate Fe values were high. This low adsorption was attributed to the blocking of adsorption sites by organic matter.

In a later study, Johnson et al. (1986) found that young, relatively unweathered Inceptisols adsorbed more sulfate than older, highly weathered Ultisols, apparently because of greater amorphous (oxalate extractable) Fe and Al in the Inceptisols. In contrast to previous findings, the authors suggested that soils high in crystalline Fe and Al

oxides will have lower anion adsorption capacities than less weathered soils with low Fe and Al oxide crystallinity. The effect of organic matter on anion adsorption in this situation was seen as positive because of its role in the maintenance of non-crystalline Fe and Al hydrous oxides.

Singh (1984b) found that removal of organic matter from a Typic Udipsamment and an Umbric Dystrochrept with H_2O_2 resulted in slightly higher sulfate adsorption in both soils. Similarly, results from work with a Cecil (Typic Hapludult) Bt1 horizon suggested that SO_4^{2-} and low molecular weight organic compounds competed for similar adsorption sites, and readily displaced each other during soil leaching experiments (Evans, 1986).

A difficulty encountered in applying laboratory results to behavior of soils under field conditions is that retention of sulfate in field plots is usually greater than that predicted from laboratory adsorption studies (Johnson et al., 1979a; Johnson and Henderson, 1979; Johnson, D.W., et al., 1981). Possible reasons for this discrepancy include increasing chemical fixation with time, effects of temperature and moisture fluctuations, soil-water contact time, and soil disturbance (Johnson et al., 1979a, Johnson, D.W., et al., 1981). Haynes (1983) observed that air-drying of a limed Spodosol soil sample increased the net negative charge and decreased subsequent adsorption of sulfate by the soil. Another reason for lower sulfate adsorption in laboratory studies is that many adsorption studies were

performed at low ionic strength and in solutions of Na_2SO_4, both factors which would tend to depress sulfate adsorption as noted by Chao et al. (1963) and Barrow (1967).

MECHANISMS OF SULFATE RETENTION IN SOILS

The primary mechanism of sulfate retention in soils involves sulfate adsorption by an anion or ligand exchange reaction with hydroxo (OH^-) and aquo (OH_2) groups associated with hydroxy Fe and Al oxides (Chao et al., 1965; Rajan, 1978). While most anions may be adsorbed non-specifically and held by electrostatic forces, anions like phosphate and sulfate are also adsorbed specifically and apparently form chemical bonds with metal atoms such as aluminum (Rajan, 1979a; 1979b). Hingston et al. (1972) postulated that specific adsorption of an anion is made possible by the presence of protons either on the oxide surface or derived from the dissociation of an acid. Rajan (1978) hypothesized that at low concentrations, sulfate displaces aquo groups from positive sites, while with increasing concentration, increasing proportions of hydroxo groups are displaced from neutral sites. Such ligand exchange adsorption of anions shifts the point of zero charge to more acid pH values, with the sesquioxide surface becoming more negative (Hingston et al., 1967; Rajan, 1979b). The formation of monodentate ligands during adsorption is thought to allow reversibility of adsorption, while the formation of bridging or multidentate ligands favors irreversibility (Hingston et

al., 1974).

Sulfate adsorption by a Cecil soil approached a maximum at a concentration of 25 meq SO_4^{2-} L^{-1} in equilibrium solution. While this may indicate that sulfate was adsorbed as an exchange reaction, certain precipitation reactions also exhibit similar maxima (Kamprath et al., 1956). In contrast, four sulfate retentive soils did not possess adsorption maxima up to 31.25 meq SO_4^{2-} L^{-1} (Chao et al., 1962a). Similarly, Johnson et al. (1979b) found that within the concentration range of 0 to 19 meq SO_4^{2-} L^{-1}, neither a tropical nor a temperate forest soil reached an adsorption maximum. The lack of adsorption maxima in such soils suggests that either anion exchange was not involved or that other mechanisms in addition to anion exchange were involved in sulfate retention (Chao et al., 1962a).

The interactions among iron, aluminum, sulfate, and pH indicate that Fe and Al hydroxy sulfate minerals also play a role in sulfate retention in soils. A variety of pure solution and soil solution studies have shown that precipitation and dissolution of aluminum and iron hydroxy sulfates are an additional mechanism for the retention and release of sulfate in acid soils (Adams and Rawajfih, 1977; Adams and Hajek, 1978; Wolt and Adams, 1979; Wolt, 1981; Weaver et al., 1985). Soil drying cycles and resultant increase in salt content would encourage retention of sulfate as aluminum hydroxy sulfate, while soil wetting would produce dilution and sulfate release (Weaver et al.,

1985). Since adsorption is often a necessary step in the initiation of a precipitation reaction, Nordstrom (1982) contended that a continuum, rather than a sharp distinction, exists between "pure adsorption" and "pure precipitation."

The possibility that aluminum and sulfate may co-precipitate or otherwise interact in soil solution is not only relevant to sulfate retention, but also to the effects of acid precipitation on solubility of aluminum in soils. Joffe and McLean (1927) observed that sulfate suppressed the solubility of aluminum in soils. Sulfate also markedly affected the precipitation of aluminum hydroxide from acid solutions, evidently by acting as a catalyst to accelerate the overall precipitation process (DeHek et al., 1978). Similarly, short term reaction of hydrous alumina and sulfate at pH 5.0 in 0.01 M NaCl resulted in aluminum concentration in the supernatant decreasing to less than 0.01 meq L^{-1} as the amount of sulfate adsorption increased (Rajan, 1978). In contrast, increasing rates of K_2SO_4 added to columns of sandy loam soil caused increasing concentrations of all soil solution ions, including aluminum (Adams and Rawajfih, 1977). Nordstrom (1982) suggested that this increase in aluminum concentration resulted from increased aluminum sulfate complexing.

Equilibrium calculations based on ionic activities in a variety of soils exposed to heavy sulfate loading indicated that the concentration of aluminum in soil solution was potentially regulated by the solubility of aluminum hydroxy

sulfates such as jurbanite ($Al(OH)SO_4$), basaluminite ($Al_4(OH)_{10}SO_4$), or alunite ($KAl_3(OH)_6(SO_4)_2$) (Van Breeman, 1973; Wolt, 1981; Nilsson and Bergkvist, 1983). In contrast, the amounts of dissolved aluminum observed in streams draining Spodosols of the Hubbard Brook Experimental Forest could be explained by the solubility of a variety of minerals, with the possible exception of $Al(OH)SO_4$ (Johnson, N.M., et al., 1981). From the information reviewed, it seems likely that under certain conditions the co-precipitation of aluminum and sulfate in soils affects both the retention of sulfate and solubility of aluminum. The importance of this interaction to acid precipitation effects remains uncertain.

Surface soils from four forested watersheds at the Coweeta Hydrologic Laboratory were found to rapidly convert added SO_4^{2-} into ester sulfate and carbon-bonded S, suggesting that incorporation of S into non-extractable organic forms was an additional mode of sulfate retention in forest ecosystems (Fitzgerald and Strickland, 1982). Subsequently, microbial transformation of sulfate to organic forms was found to be an important influence on sulfate accumulation and mobility in both surface (O,A) horizons and underlying B horizons in a variety of forest soils (David et al., 1982; David et al., 1983; Swank et al., 1984; Strickland et al., 1986; Schindler et al., 1986). Based on these findings, Schindler et al. (1986) suggested that the combined effects of biological incorporation and physico-

chemical sulfate adsorption need to be considered when assessing the impact of elevated sulfate inputs on cation loss from forest soils.

APPLICATION TO PRESENT STUDY

The preceding review indicated a variety of factors and soil properties are related to sulfate adsorption in soils. Factors affecting sulfate adsorption included pH, type of cation present, presence of competing anions, extractable Al and Fe fractions, extractable sulfate, organic carbon, clay content, and soil horizon type. By inference, soils that differ in these soil properties should also differ in sulfate adsorption ability.

Preliminary studies examining effects of air-drying on sulfate adsorption in selected Michigan forest soils are described in Chapter III. Literature reports of soil properties shown to affect sulfate adsorption guided selection of the types and methods of soil analyses performed in the present study (Chapter IV). Comparisons of sulfate adsorption and extractable sulfate within and between representative Michigan soil series are presented in Chapter V. Relationships of soil properties to sulfate adsorption in Michigan forest soils are addressed in Chapter VI. Use of selected soil properties as variables in multiple regression equations to predict sulfate adsorption is examined in Chapters VII and VIII.

Chapter III

PRELIMINARY LABORATORY STUDIES

Air-drying of soil samples is a possible source of discrepancy between laboratory and field studies of sulfate adsorption. Preliminary studies were performed to determine the effect of air-drying on sulfate adsorption in selected soils, to provide data on differences in sulfate adsorption between soil horizons, and to develop adsorption isotherms for some of the soil horizons studied.

SOIL SAMPLING AND DESCRIPTION

Three pedons were sampled, representing the Grayling, Kalkaska, and Montcalm series. Soils were sampled in August and September, 1984, in Montmorency County, Michigan. Two pedons, Grayling and Montcalm, were located in Section 34, T32N, R3E in a mixed red and jack pine plantation. The Kalkaska pedon was located in Section 29, T31N, R2E, in a northern hardwoods stand. Samples from each mineral horizon were taken from soil pits and sealed in polyethylene bags. One half of each composite sample was air-dried at 25 ^{o}C and passed through a 2 mm sieve. The field-moist half of each sample was forced through a 2 mm sieve with a neoprene stopper, double-bagged in polyethylene bags, and refrigerated prior to analysis. Descriptions of the sampled pedons are given below.

GRAYLING (mixed, frigid Typic Udipsamments)

A/E - 0 to 4 cm; black (N 2/0) (A) and light gray (10YR 7/1) (E) sand; weak medium granular structure; very friable; many fine roots; abrupt smooth boundary.

Bw1 - 4 to 14 cm; strong brown (7.5YR 4/6) sand; weak medium granular structure; very friable; many fine and medium roots; clear smooth boundary.

Bw2 - 14 to 33 cm; strong brown (7.5YR 4/6) sand; single grain; loose; common fine roots; 1% gravel; gradual smooth boundary.

BC - 33 to 65 cm; yellowish brown (10YR 5/6) sand; single grain; loose; few fine roots; 1% gravel; diffuse wavy boundary.

C - 65 to 160 cm; light brown (7.5YR 6/4) sand; single grain; loose; few medium and fine roots; 1% gravel.

KALKASKA (sandy, mixed, frigid Typic Haplorthods)

A - 0 to 4 cm; black (N 2/0) loamy sand; weak medium granular structure, very friable; many fine roots; abrupt smooth, discontinuous boundary.

E - 0 to 7 cm; grayish brown (10YR 5/2) loamy sand; weak medium granular structure; very friable; many fine and medium roots; abrupt wavy boundary.

Bh - 7 to 19 cm; dark reddish brown (5YR 3/3) loamy sand; moderate medium subangular blocky structure; friable; some fragments of cemented ortstein present; common medium and large roots; clear wavy boundary.

Bs1 - 19 to 46 cm; strong brown (7.5YR 4/6) loamy sand; weak medium granular structure; very friable; some fragments of cemented ortstein present; common medium and large roots; clear irregular boundary.

Bs2 - 46 to 80 cm; dark yellowish brown (10YR 4/6) loamy sand; weak medium granular structure; very friable; few medium roots; gradual irregular boundary.

BC - 80 to 124 cm; light brown (7.5YR 6/4) loamy sand; weak medium subangular blocky structure; very friable; few medium roots; gradual smooth boundary.

C - 124 to 174 cm; light brown (7.5YR 6/4) loamy sand; single grain; loose; with few thin (0.5 to 1 cm) bands of yellowish red (5YR 4/6) sandy loam (Bt); moderate medium subangular blocky structure; firm.

MONTCALM (coarse-loamy, mixed, frigid Eutric Glossoboralfs)

A - 0 to 4 cm; black (N 2/0) loamy sand; weak medium granular structure; very friable; many fine and medium roots; clear wavy boundary.

E - 4 to 16 cm; light brownish gray (10YR 6/2) loamy sand; weak medium granular structure; very friable; many medium roots; abrupt wavy boundary.

Bs - 16 to 66 cm; strong brown (7.5YR 4/6) loamy sand; weak fine subangular blocky structure; very friable; common medium and large roots; gravel band near lower boundary; gradual smooth boundary.

E' - 66-90 cm; brown (10YR 5/3) loamy sand; moderate medium platy structure; firm; few medium roots; some patchy clay films present; clear wavy boundary.

E' and Bt - 90 to 150 cm; pale brown (10YR 6/3) sand (E'); single grain; loose; in 2 to 10 cm thick layers and lenses; and yellowish red (5YR 4/6) sandy clay loam (Bt); moderate coarse subangular blocky structure; firm; in 2 to 30 cm thick bands and lenses; few medium roots; clear irregular boundary.

2C - 150 to 180 cm; brown (7.5YR 5/4) sandy clay loam; moderate medium subangular blocky structure; friable; few fine and medium roots; strong effervescence.

EXPERIMENT 1 - MONTCALM LOAMY SAND

The Montcalm series consists of deep well-drained soils formed in sandy and loamy materials on moraines and outwash plains (SCS-USDA). The Montcalm pedon sampled was selected for detailed study because of its combination of soil horizons that differ in physical and chemical properties related to sulfate adsorption.

Methods

This preliminary study of sulfate adsorption employed a factorial arrangement of treatments in a randomized complete

block design. The three factors incorporated were sample preparation (air-dry, field-moist), solution sulfate concentration (2.5, 5.0, 10.0, 25.0, 50.0, 100.0 mg S L^{-1}), and soil horizon (A, E, Bs, E', Bt, 2C). The SO_4-S concentration range from 2.5 to 25.0 mg S L^{-1} approximated concentrations in soil solution and groundwater under forest soils in northern lower Michigan (Urie et al., 1986). The 50.0 and 100.0 mg S L^{-1} levels allowed for examination of sulfate adsorption at higher than ambient concentrations. The experiment was conducted in three blocks to account for possible day-to-day variations in laboratory technique. Sulfate adsorption was determined by equilibrating soil samples with 0.01 M $CaCl_2$ containing the graded concentrations of SO_4-S added as Na_2SO_4. Ten-gram samples were shaken in 50 mL of solution for 24 hours, filtered through Whatman # 42 filter paper, and analyzed for SO_4-S by automated $BaSO_4$ turbidimetry (Wall et al., 1980). Sulfate adsorption, adjusted to oven-dry soil weight, was calculated from disappearance of sulfate from solution.

Statistical analysis followed procedures outlined for factorial experiments by Steel and Torrie (1980). Mean separation for analysis of variance results was accomplished using Tukey's w procedure (Steel and Torrie, 1980). Due to high variability in certain horizons, data from 50.0 and 100.0 mg S L^{-1} were excluded from an overall analysis of variance. Remaining data (mg S kg^{-1} soil) were transformed to a natural log (ln) scale to control variance.

Transformation of positive data (S adsorption) took the form $\ln[(\text{mg S kg}^{-1})+1]$ and transformation of negative data (S release) took the form $-[\ln(|\text{mg S kg}^{-1}|+1)]$. This manipulation gave equal values on a log scale to positive and negative numbers equidistant from zero, a negative sign denoting numbers below zero on the original scale of measurement. Addition of one to all absolute values prior to taking logs eliminated negative logs for values less than one, and maintained a zero point as $\ln(0+1) = 0$.

Results and Discussion - Experiment 1

Results of the analysis of variance are given in Table 3.1. The three-way interaction was not significant and was pooled with error. Significant two-way interactions were present between all three factors.

Table 3.1

Analysis of Variance Results - Montcalm Loamy Sand

Source	DF	SS	MS	F	P
Block	2	3.3522	1.6761	17.77	0.000
Soil Preparation	1	1.0363	1.0363	10.99	0.005
Soil Horizon	5	395.3932	79.0786	838.31	0.000
SO_4-S Concentration	3	8.8064	2.9354	31.12	0.000
SP x SH	5	6.9032	1.3806	14.64	0.000
SP x SC	3	1.9357	0.6452	6.84	0.003
SH x SC	15	24.2982	1.6199	17.17	0.000
Error	109	10.2821	0.0943		

Figure 3.1 shows that A and E horizons released sulfate during equilibration, while Bs, E', and Bt horizons adsorbed sulfate. Similar patterns of desorption and adsorption have been reported for other acid forest soils (Singh, 1980b; Johnson and Todd, 1983; Fuller et al., 1985; Weaver et al., 1985). The overall trend was similar for both air-dry and field-moist samples, but significant differences existed within E, Bs, and 2C horizons. Air-dry E horizons released more sulfate, and air-dry Bs horizons adsorbed more sulfate than corresponding field-moist samples. Air-dry 2C horizon samples released sulfate, but field-moist 2C samples adsorbed sulfate. Drying effects on the 2C horizon were important because field-moist samples gave a totally different impression of sulfate adsorption ability than air-dry samples. Differences between horizons are likely due to differences in organic matter, Fe and Al content, clay content, and pH (Barrow, 1967; Singh, 1980b; Johnson and Todd, 1983; Fuller et al., 1985; Evans, 1986). Response to air-drying apparently differs according to differential drying effects on soil properties.

Figure 3.2 demonstrates the divergence between air-dry and field-moist samples as sulfate concentration increases. Air-dry and field-moist samples were not different at 2.5, 5.0, and 10.0 mg S L^{-1}, but were significantly different at 25.0 mg S L^{-1}. The divergence reflects lower S release from field-moist A and E horizons as well as an increase in S adsorption by field-moist E', Bt, and 2C horizons.

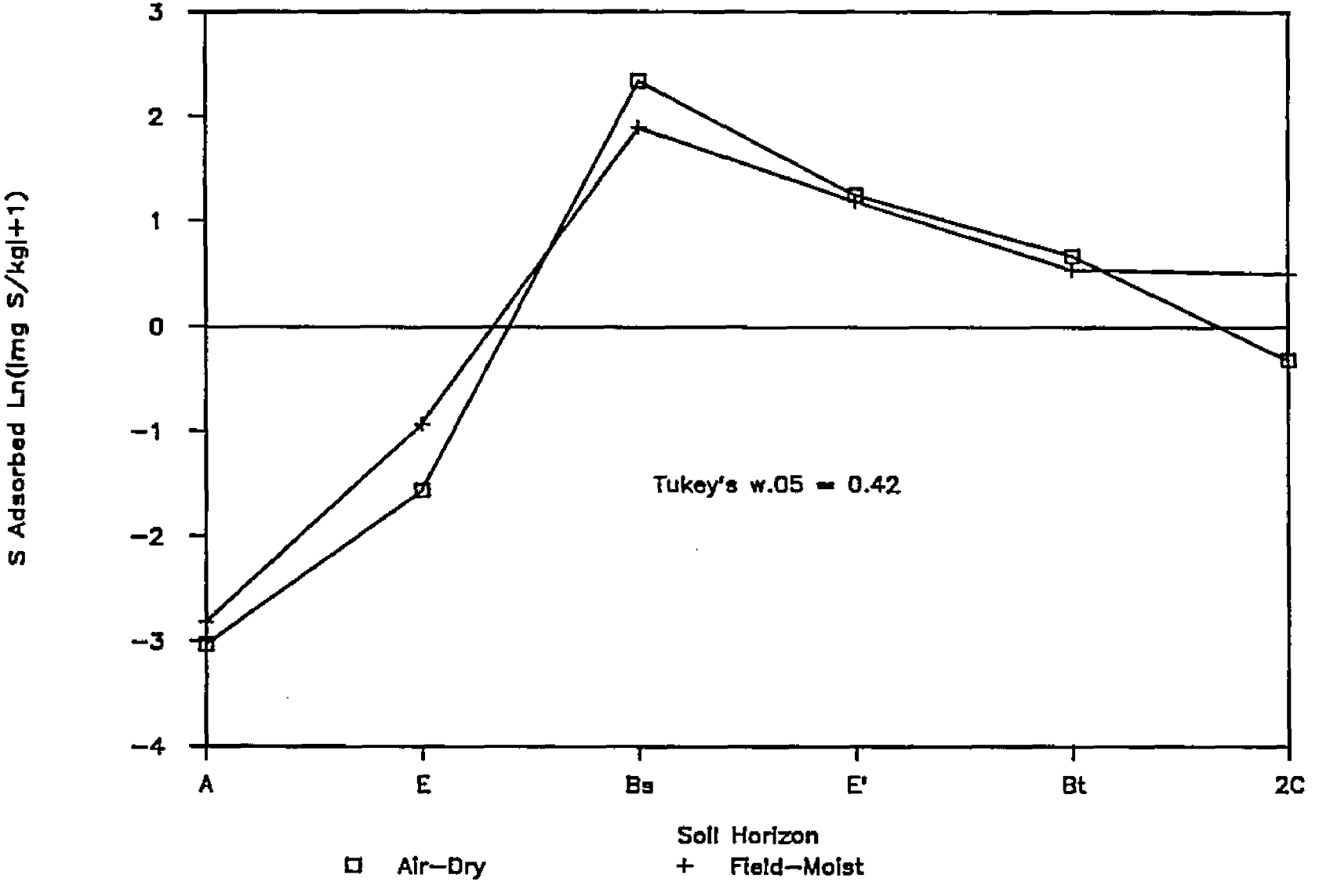

Figure 3.1

Soil Preparation x Soil Horizon Interaction - Montcalm Loamy Sand

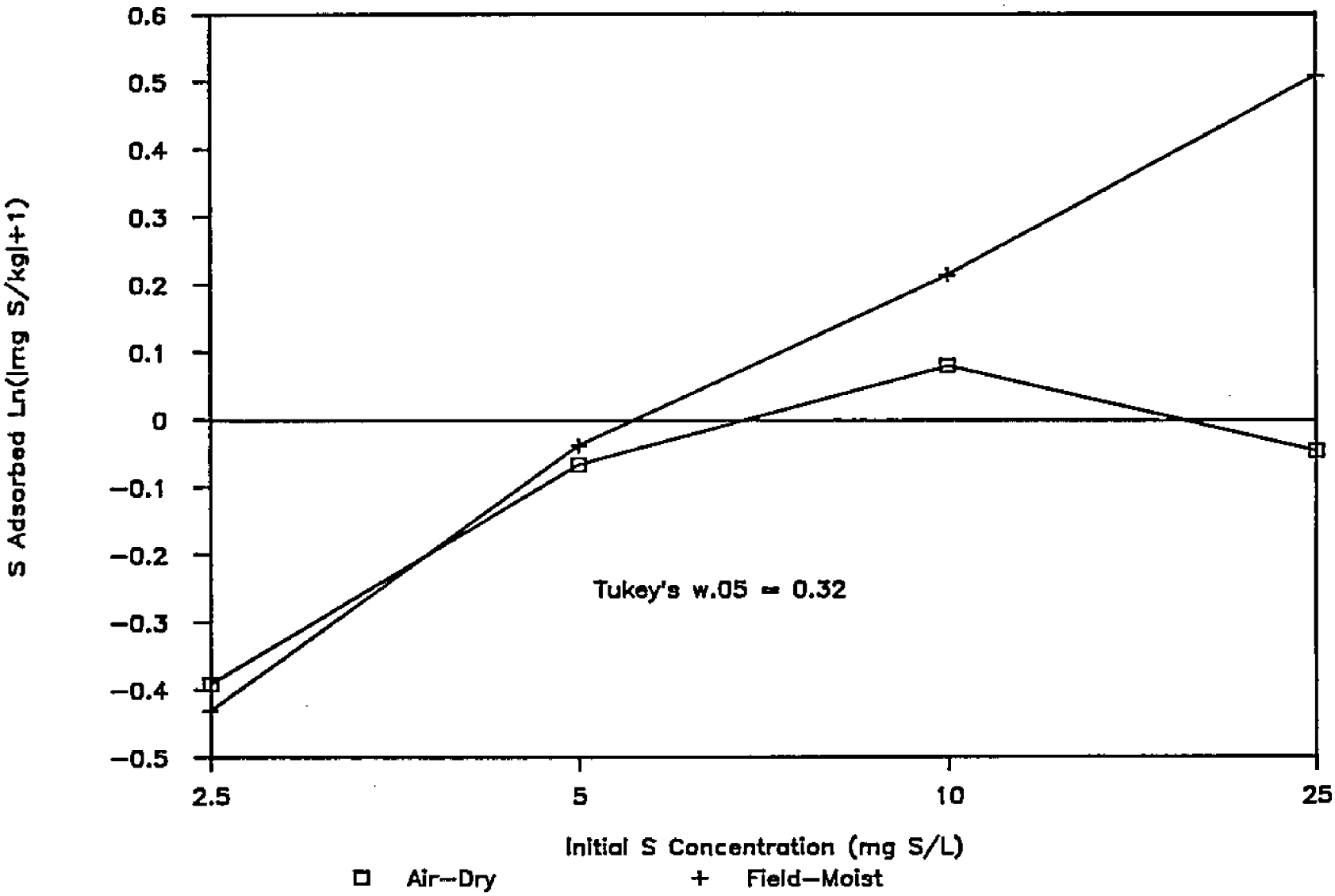

Figure 3.2

Soil Preparation x Sulfate Concentration Interaction - Montcalm Loamy Sand

Figure 3.3 shows the pattern of S adsorption or release for each horizon in relation to initial SO_4-S concentration in solution. Sulfate adsorption increased with solution sulfate concentration in Bs, E', Bt, and 2C horizons, while sulfate release increased for A and E horizons. The rate of increase in S adsorption was similar for 2C, E', and Bs horizons, while rate of increase in the Bt horizon was greater, possibly related to the higher clay content of the Bt horizon. Increased sulfate release from A and E horizons may be an artifact of increasing Na^+ concentration with increasing S concentration (meq ratio of Na^+/Ca^{2+} increased from 0.008 at 2.5 mg S L^{-1} to 0.078 at 25.0 mg S L^{-1}).

The interaction between soil preparation and SO_4-S concentration was investigated further by conducting separate analyses of variance for each soil horizon, including all six sulfate concentrations (Appendix D, Table D.1). Data were transformed as described previously. Significant interactions were present for A, E', and 2C horizons (Figure 3.4), but not for E, Bs, or Bt horizons (Figure 3.5). Interaction was especially apparent in the 2C horizon where field-moist samples adsorbed sulfate between 10.0 and 100.0 mg S L^{-1}, while air-dry samples varied around zero (Figure 3.4). Occurrence of sulfate adsorption in the field-moist 2C horizon was surprising because of its high pH (Table 3.2), although results presented by Bolan et al. (1986b) showed some sulfate adsorption to occur in soils with pH adjusted to similar values. Co-precipitation of

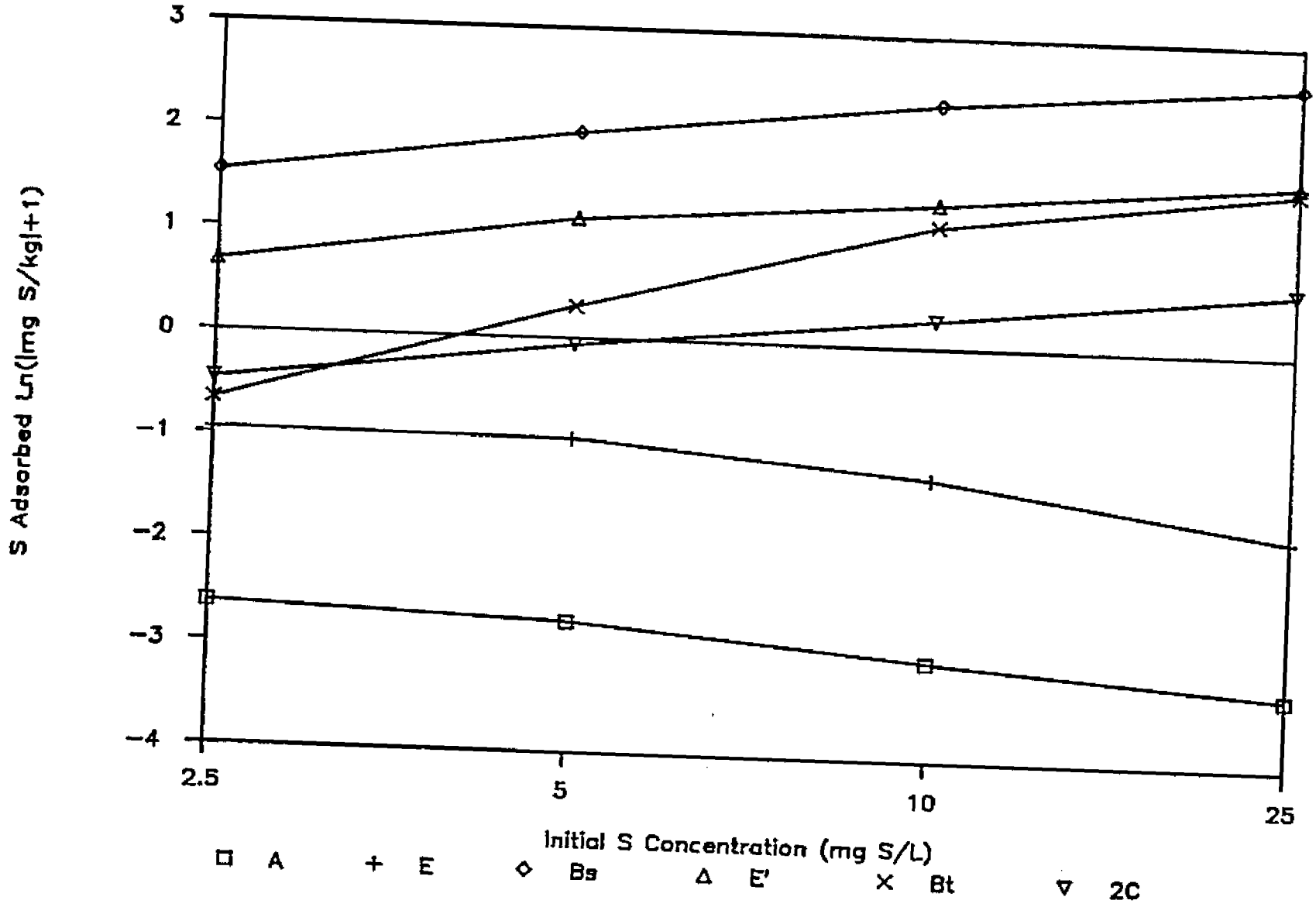

Figure 3.3

Soil Horizon x Sulfate Concentration Interaction - Montcalm Loamy Sand

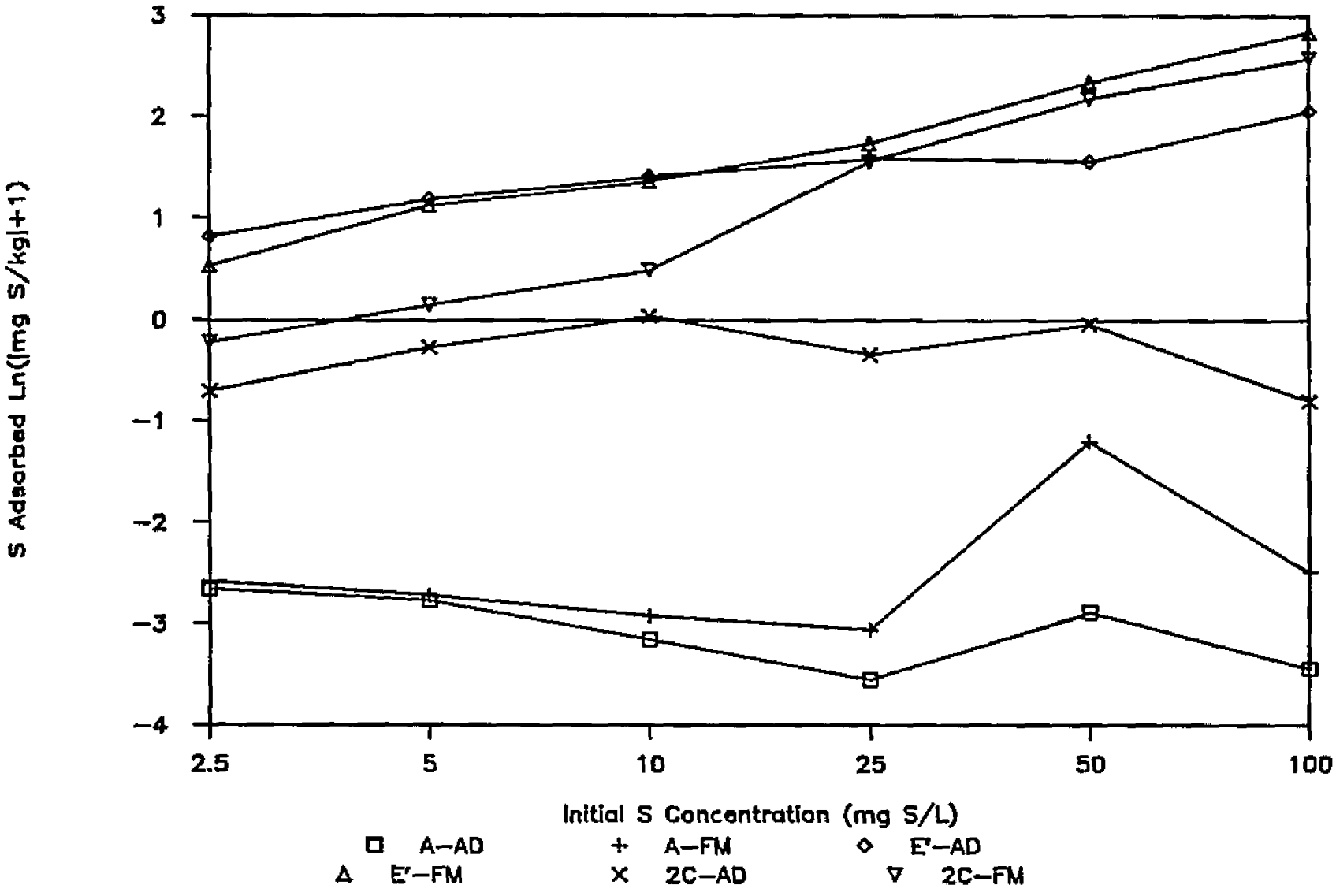

Figure 3.4

Horizons with Air-Dry x Field-Moist Interactions - Montcalm Loamy Sand

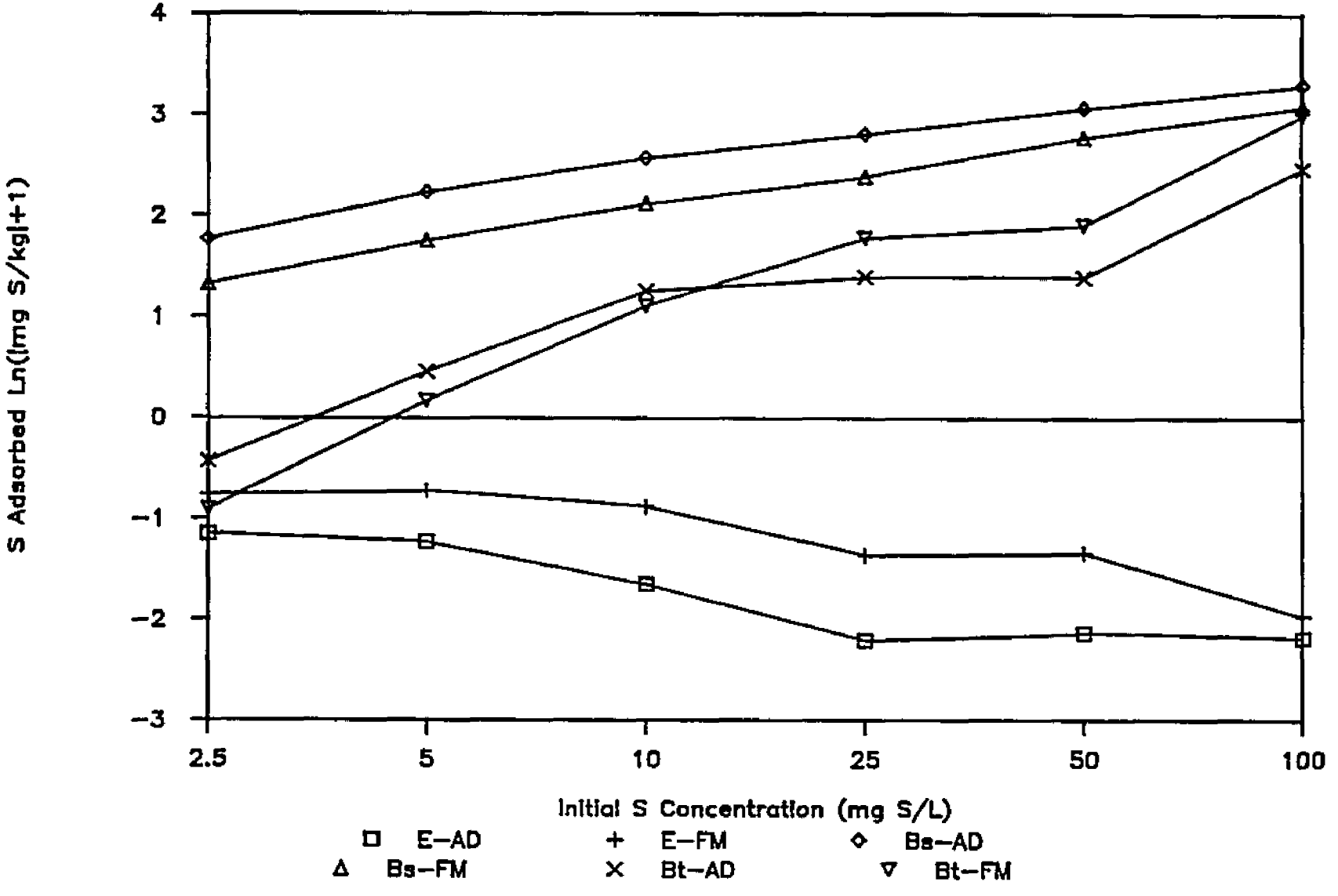

Figure 3.5

Horizons without Air-Dry x Field-Moist Interactions - Montcalm Loamy Sand

sulfate with $CaCO_3$ may be involved (Williams and Steinbergs, 1962). The Bs adsorption curves (Figure 3.5) are similar to ones determined by Singh (1980a) for Bs and Bw horizons of Norwegian Udipsamments and Dystrochrepts. The abrupt slope changes evident in E' (Figure 3.4) and Bt (Figure 3.5) horizon adsorption curves are similar to changes in adsorption curves found by Johnson and Cole (1977) and Haque and Walmsley (1973) at comparable sulfate concentrations. Breaks in A and E horizon sulfate release curves were apparent between 25.0 and 50.0 mg S L^{-1}. The 50.0 and 100.0 mg S L^{-1} solutions were diluted prior to analysis and the breaks may be due to reduction in organic matter interferences in the analysis.

In A and E horizons, air-drying encouraged sulfate release, possibly due to mineralization of organic S during drying. Increased release of inorganic sulfur from air-dry soil as compared to field-moist soil was also reported by Freney (1958), Barrow (1961), Williams and Steinbergs (1964), Williams (1967), and Tabatabai and Bremner (1972). David et al. (1982), found that drying caused increases in extractable sulfate in organic horizons, but decreases in mineral horizons, of a Typic Fragihumod. In the Montcalm Bs horizon, air-drying promoted sulfate adsorption, possibly through disintegration of soil aggregates or disruption of organic matter-sesquioxide bonds, making an increased number of anion adsorption sites available. Air-drying has also been found to increase P adsorption in soils (Bartlett and

James, 1980; Olsen and Court, 1982). Sulfate adsorption at higher solution sulfate concentrations tended to be lower in air-dry E', Bt, and 2C samples than in field-moist samples. This suggests that drying produced changes in the nature of amorphous hydroxy Al polymers, clay minerals or in the charge of adsorption sites that would inhibit adsorptive capacity (Haynes, 1983). Within horizons, differences in pH between air-dry and field-moist samples were minor (Table 3.2), suggesting that pH changes did not cause the differences in sulfate adsorption.

Table 3.2

Soil pH of Air-Dry and Field-Moist Samples

	pH - H_2O		pH - $CaCl_2$	
Horizon	Air-Dry	Field-Moist	Air-Dry	Field-Moist
A	4.05	4.39	3.34	3.57
E	4.39	4.68	3.59	3.66
Bs	5.90	5.96	4.76	4.68
E'	6.25	6.42	4.97	5.02
Bt	6.57	6.99	6.32	6.30
2C	8.39	8.48	7.72	7.72

Adsorption Isotherms - Experiment 1

Adsorption data from the Bs, E', Bt, and 2C horizons were fitted to the Freundlich and Langmuir isotherms, two equations commonly used to numerically summarize the adsorption characteristics of a soil (Singh, 1984a). The

linear form of the Freundlich equation is log X = log A + B(log C), where X = sulfate adsorbed (mg S kg^{-1}), C = equilibrium sulfate concentration (mg S L^{-1}), and A and B are empirical coefficients (Singh, 1984a). The linear form of the Langmuir equation is C/X = C/A + 1/BA, where A = adsorption maximum (mg S kg^{-1}), B is a constant related to adsorption energy (Parfitt, 1978), C = equilibrium sulfate concentration (mg S L^{-1}), and X = S adsorbed (mg S kg^{-1}). For adsorption curves that conform to the Langmuir isotherm, a plot of C/X against C gives a straight line of slope 1/A, from which A may be calculated and the constant B obtained from the intercept (Parfitt, 1978).

Results of fitting data from the Montcalm loamy sand to the Freundlich and Langmuir equations are presented in Table 3.3. Application of the Freundlich equation to Bt and 2C horizon data, where negative values existed, required transformation of S adsorption data to the form (+,-) log(|mg S kg^{-1}|+1), a minus sign denoting the log of numbers below zero. For Bt and 2C horizons, use of the linear form of the Freundlich equation is necessary to avoid confusion over appropriate values to assign negative numbers.

Both Freundlich and Langmuir equations appeared to describe Bs horizon adsorption data adequately (r^2 = .938 to .959). Comparable r^2 values for Freundlich (r^2 = .978 to .996) and Langmuir (r^2 = .878 to .996) equations were reported for Bs and Bw horizons of similar soils by Singh (1984a).

Table 3.3

Estimated Parameters for Freundlich and Langmuir Isotherms

	Freundlich			Langmuir		
Horizon	Slope (B)	Intercept (LogA)	r^2	Slope (1/A)	Intercept (1/BA)	r^2
Bs - AD†	0.3839	0.6820	0.951	0.0357	0.3971	0.959
Bs - FM‡	0.4987	0.3419	0.954	0.0409	0.9145	0.938
E' - AD	0.3717	0.0517	0.671	0.1510	2.4136	0.678
E' - FM	0.7859	-0.3538	0.850	0.0394	3.3720	0.280
Bt - AD††	0.6540	-0.3050	0.720	----	----	0.145
Bt - FM	0.9766	-0.6563	0.864	----	----	0.146
2C - AD	----	----	0.001	----	----	0.007
2C - FM	0.8079	-0.4757	0.805	----	----	0.043

† AD = air-dry samples
‡ FM = field-moist samples
†† Freundlich isotherm for Bt and 2C horizons, log(X) = (+,-) log(|mg S kg^{-1}|+1)

The Langmuir isotherm predicted an estimated adsorption maximum of 28.0 mg S kg^{-1} for air-dry Bs samples and 24.4 mg S kg^{-1} for field-moist Bs samples. Adherence to the Langmuir isotherm worsened in the E' horizon and was not significant in the Bt and 2C horizons. Examination of residuals indicated that the Freundlich equation provided the best fit to data for Bs and E' horizons, while the Langmuir equation suffered from systematic over-estimation at low and high sulfate concentrations and under-estimation at intermediate sulfate concentrations. Singh (1984a) found that the Langmuir isotherm exhibited similar lack of fit at

comparable sulfate concentrations when applied to B horizons of Udipsamments. Based on comparisons of residual sums of squares, F values, and examination of residuals, Singh (1984a) concluded that the Freundlich equation was best for describing sulfate adsorption in B horizons of acid forest soils. This conclusion is supported by the results of the present study. Based on r^2 values (Table 3.3), adsorption by field-moist samples adhered more closely to the Freundlich isotherm than adsorption by air-dry samples. Freundlich equations describing adsorption by field-moist samples had lower Y-intercepts and steeper slopes than equations for air-dry samples, differences in slope and intercept being significant for E', Bt, and 2C horizons. These differences reflect interactions between air-dry and field-moist samples discussed earlier.

EXPERIMENT 2 - GRAYLING AND KALKASKA SERIES

A second, smaller experiment was performed using samples from the Grayling and Kalkaska pedons. Both series are well- to excessively drained soils formed in sandy glacial deposits of Wisconsinan age (SCS-USDA). These two series represent extremes in spodic development, Grayling lacking a spodic horizon and Kalkaska possessing a strongly developed spodic horizon high in organic carbon.

Methods

A factorial arrangement was employed in a randomized complete block design. Factors were soil series (Grayling, Kalkaska), soil preparation (air-dry, field-moist), soil horizon (Grayling: Bw1, Bw2, BC; Kalkaska: Bh, Bs1, Bs2), and sulfate concentration (5.0, 25.0 mg S L^{-1}). The experiment was conducted in three blocks. Adsorption equilibrations were performed as described previously. Data were transformed to ln(|mg S kg^{-1}|+1), with a negative sign applied to logs of negative numbers.

Results and Discussion - Experiment 2

Analysis of variance indicated significant main effects and interactions between series and soil horizon and between soil preparation and soil horizon (Appendix D, Table D.2). An examination of the Series x Soil Horizon interaction (Figure 3.6) shows that the Grayling Bw1 released sulfate, while the Kalkaska Bh had significantly greater capacity to adsorb sulfate. This difference was apparently related to degree of spodic development, chemical properties associated with the Kalkaska Bh horizon favoring sulfate adsorption. The second and third Grayling (Bw2, BC) and Kalkaska (Bs1, Bs2) horizons tested were similar morphologically and displayed similar sulfate adsorption abilities. Because of the Series x Soil Horizon interaction, further investigation of main effects or interactions combining both series was misleading and separate analyses of variance were performed for each series. Analysis of variance results for the

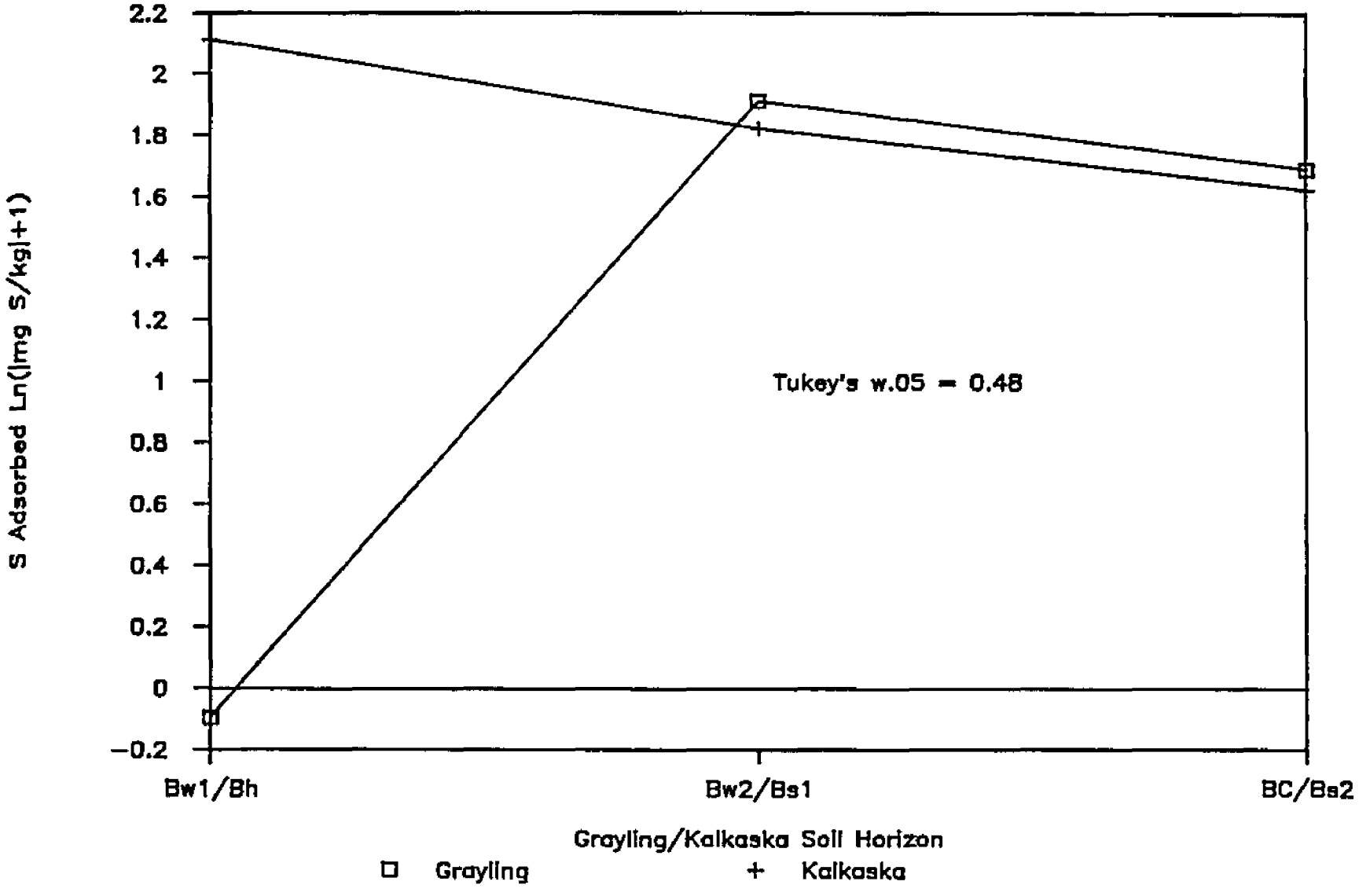

Figure 3.6

Series x Soil Horizon Interaction - Grayling and Kalkaska Pedons

Grayling pedon are presented in Table 3.4. With the Exception of the Soil Preparation x Soil Horizon interaction, two-way and three-way interactions were non-significant and were pooled with error.

Table 3.4

Analysis of Variance Results - Grayling Sand

Source	DF	SS	MS	F	P
Block	2	0.4413	0.2206	0.86	0.434
Soil Preparation	1	0.0307	0.0307	0.12	0.663
Soil Horizon	2	29.0770	14.5385	56.50	0.000
SO_4-S Concentration	1	5.3104	5.3104	20.64	0.000
SP x SH	2	2.0970	1.0485	4.08	0.030
Error	27	6.9473	0.2573		

The main effect of increasing solution sulfate concentration was significant, with adsorption increasing with S concentration. The interaction between soil preparation and soil horizon is shown in Figure 3.7. For the Grayling Bw1 horizon, air-dry samples released S, while field-moist samples adsorbed S. In contrast, both air-dry Bw2 and BC horizons had higher sulfate adsorption than corresponding field-moist samples. Bw1 samples were significantly lower in S adsorption than Bw2 or BC samples.

Analysis of variance results for the Kalkaska pedon are presented in Table 3.5. Two-way and three-way interactions were not significant and were pooled with error. All three

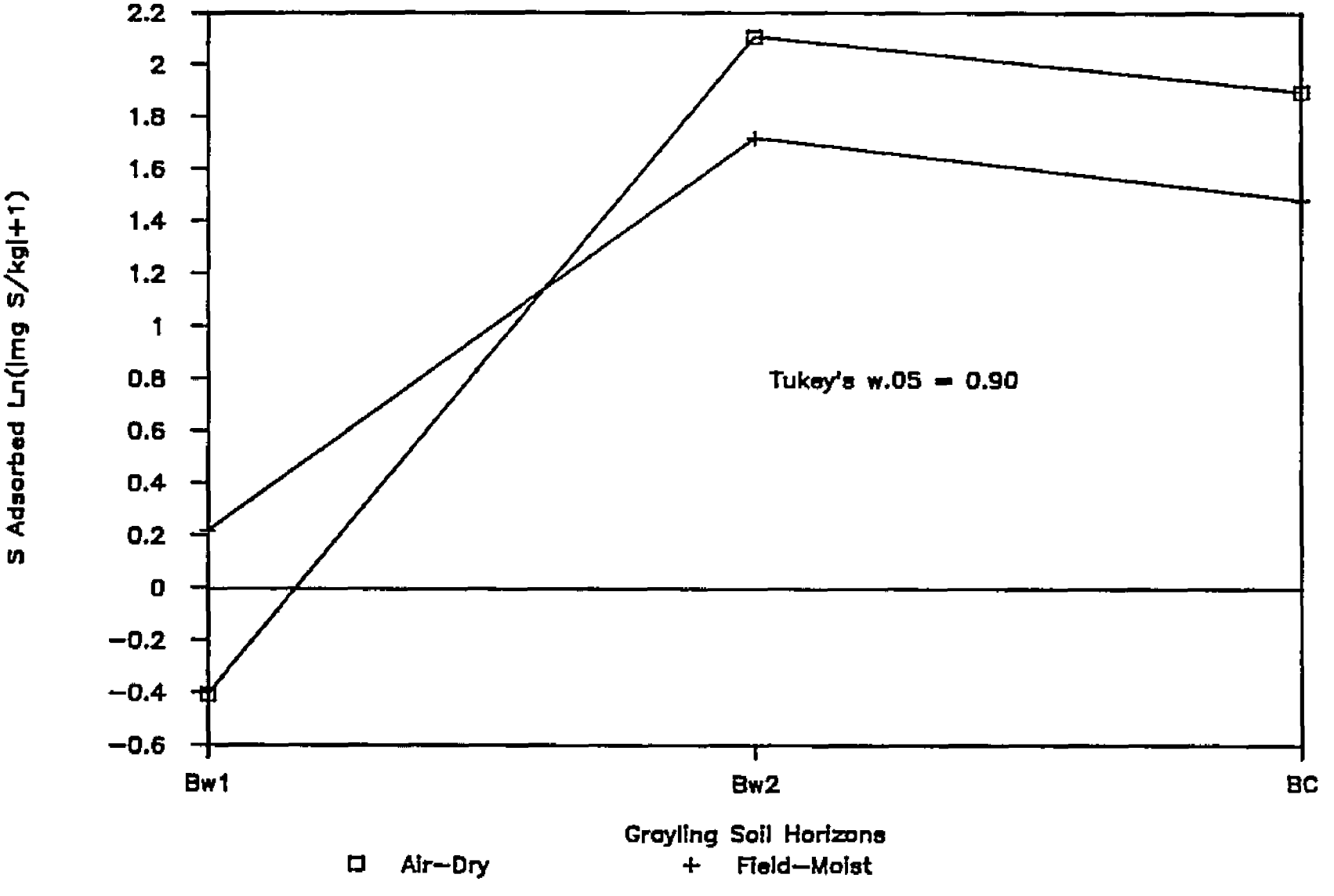

Figure 3.7

Soil Preparation x Soil Horizon Interaction - Grayling Sand

main effects were significant. Air-dry samples adsorbed more sulfate than field-moist, and sulfate adsorption was significantly different between horizons, increasing in the order Bs2 < Bs1 < Bh. Sulfate adsorption increased with increasing sulfate concentration in solution.

Table 3.5

Analysis of Variance Results - Kalkaska Loamy Sand

Source	DF	SS	MS	F	P
Block	2	0.0949	0.0474	0.91	0.414
Soil Preparation	1	1.4344	1.4344	27.64	0.000
Soil Horizon	2	1.4640	0.7320	14.10	0.000
SO_4-S Concentration	1	4.7558	4.7558	91.63	0.000
Error	29	1.5048	0.0519		

Lower sulfate adsorption by field-moist Grayling Bw2 and BC and by Kalkaska Bh, Bs1, and Bs2 horizons was similar to results obtained for the Montcalm Bs horizon. Air-dry Grayling Bw1 horizon samples released sulfate while field-moist Bw1 samples adsorbed sulfate, similar to greater sulfate release by the air-dry Montcalm E and 2C horizons. The Grayling Bw1 had weak sulfate adsorption properties in comparison with other Grayling and Kalkaska soil horizons. This suggests that in horizons with weak adsorption abilities, air-drying will further reduce the ability to adsorb sulfate or cause sulfate release. In horizons with stronger adsorption abilities (Bh, Bs, Bw2, BC), air-drying

will increase sulfate adsorption. In horizons with intermediate adsorption abilities (E', Bt), interaction may occur with air-dry samples adsorbing more sulfate than field-moist at low S concentrations but adsorbing less sulfate than field moist at higher concentrations.

Correlations between sulfate adsorbed by air-dry and field-moist samples (paired within experimental blocks) for combined Montcalm, Grayling, and Kalkaska untransformed data are presented in Table 3.6. Significant ($P < 0.01$) correlations were present between air-dry and field-moist samples at all solution sulfate concentrations and for a variety of soil horizons. Highest correlations existed at solution concentrations of 25 mg S L^{-1} and below, while correlations deteriorated at higher sulfate concentrations or when data for all concentrations were grouped together.

Table 3.6

Correlations Between Air-Dry and Field-Moist Samples

	Initial Solution SO_4-S Concentration (mg S L^{-1})						
	2.5	5.0	10.0	25.0	50.0	100.0	2.5 to 100.0
r	0.98	0.97	0.98	0.97	0.85	0.84	0.82
n	18	36	18	36	18	18	144

SUMMARY AND CONCLUSIONS

In the soils examined, effects of air-drying of soil samples on sulfate adsorption depended on the horizon involved and the concentration of sulfate in the equilibrating solution. Air-dry samples from horizons with weak adsorptive abilities (E, Bw1, 2C) released more sulfate than field-moist samples from the same horizons. Horizons with stronger sulfate adsorption characteristics (Bh, Bs, Bw2, BC) adsorbed more sulfate after air-drying than if samples were kept field-moist. Differences in sulfate adsorption between air-dry and field-moist samples were least and correlations between soil preparations highest at solution concentrations of 25 mg S L^{-1} or less. Results suggest that laboratory studies using air-dry samples to determine relative sulfate adsorption abilities of various soils should be performed at SO_4-S concentrations below 25 mg S L^{-1} to reduce discrepancies related to air-drying. Based on these results, sulfate adsorption studies reported in subsequent chapters were performed using air-dry samples and an initial sulfate concentration of 10 mg S L^{-1}. Over the range of sulfate concentrations studied (2.5 to 100.0 mg S L^{-1}), the Freundlich equation best described sulfate adsorption isotherms in subsurface horizons of the forest soils investigated. Results suggest that development of sulfate adsorption isotherms including solution concentrations greater than 25 mg S L^{-1} might best be performed using field-moist samples.

Chapter IV

MATERIALS AND METHODS

This chapter discusses selection of soil series for study, selection of sampling locations, and field sampling methods employed. Brief composite descriptions of the profile morphologies of the soil series sampled are presented. Laboratory analytical methods are described, and general methods of statistical analysis are introduced.

SOIL SERIES STUDIED

The objectives of this study called for sampling a representative group of Michigan forest soils to determine their adsorption abilities and extractable sulfate contents, as well as to relate adsorptive abilities to other soil properties. The soil population of interest was that group of forest soils considered potentially susceptible to adverse effects from acid deposition. An investigation of the sulfate adsorption abilities of the over seventy Michigan soil series thought sensitive to acid deposition would be prohibitive in both time and expense. Therefore, a subset of soil series was selected for detailed study using the following criteria:

1. The series is classified as sensitive or slightly sensitive to acid deposition, following the criteria proposed by McFee (1980) (Appendix A).

2. The series is representative of a taxonomic group important as a forest soil in the lower peninsula of Michigan, i.e., moderate to large in extent, with a significant percent of its area in forest cover (SCS-USDA).

3. The series represents a discrete point in the soil continuum (Figure 1.1), with unique soil physical and chemical properties that affect sulfate adsorption.

Soil series selected for study were Grayling (Typic Udipsamments), Rubicon (Entic Haplorthods), Kalkaska (Typic Haplorthods), Montcalm (Eutric Glossoboralfs), Oshtemo (Typic Hapludalfs), and Spinks (Psammentic Hapludalfs). As portrayed in Figure 1.1 (Chapter I), selection of series for sampling was based within a framework of soil taxonomic relationships. The purpose of stratification over soil taxonomic groups was to provide a meaningful sample of soils with widely varying chemical and physical properties that affect sulfate adsorption (Chapter II). The Grayling, Rubicon, and Kalkaska series represented an entic-spodic gradient of soil development typified by an increase in sesquioxides and organic carbon accumulations in upper B horizons. Morphologically, Grayling has the least developed spodic character and Kalkaska the strongest. The Grayling, Spinks, and Oshtemo series represented an entic-alfic gradient of soil development, characterized by an increase in clay content and expression of the argillic horizon. Morphologically, Grayling is least developed, having little clay in its B horizons, and Oshtemo is most strongly

developed, having a vertically continuous argillic horizon present in its subsurface horizons. The Kalkaska, Montcalm, and Oshtemo series represent a spodic-alfic gradient of soil development. Spodic development is greatest and alfic development least in the Kalkaska series, while alfic development is greatest and spodic development least in the Oshtemo series. Grayling, Rubicon, Kalkaska, and Montcalm are classified as frigid zone soils, having a mean annual soil temperature lower than 8 ^{o}C. Spinks and Oshtemo are classified as mesic zone soils, having a mean annual soil temperature of 8 ^{o}C or higher, but lower than 15 ^{o}C.

Replication within series was incorporated to allow statistical comparisons between series. Based on series variability determined from available soil characterization data (SCS-USDA, 1980; MTU-FFC, 1982-1984), it was estimated (Steel and Torrie, 1980) that sampling six pedons of each series would allow statistical detection of major differences in soil chemical properties, and thus sulfate adsorption, between series. The combination of six series and six pedons per series gave a target of 36 pedons to be sampled. This number was considered a practical maximum given the available time, personnel, funding, and other resources available to complete the study.

SELECTION OF SAMPLING LOCATIONS

A soil map unit representing a selected series was considered for sampling only if it was currently forested

and the existing stand was 40 years old or older. The age qualification was adopted to reduce the effects of recent disturbance on soil chemical properties. Inclusion of any forest cover type considered typical of the series was allowed. Sampling locations were restricted to Federal, State, University, or other public lands in the lower peninsula of Michigan where permission to sample could be readily obtained. This placed little restriction on selection of locations in northern lower Michigan where extensive areas of public lands exist, but imposed fairly tight restrictions on sampling in southern lower Michigan where public lands are limited in extent.

A major purpose of sampling was to obtain soil samples on which to base correlation and regression analyses relating sulfate adsorption to other soil properties. Correlation and regression require random sampling of individuals on which pairs of measurements are made (Steel and Torrie, 1980; Draper and Smith, 1980). The stratification of sampling over soil series and soil horizons provided a range of X values. To assure that a random sample of Y values was obtained, sampling sites were selected as described below.

Counties that contained areas of the selected soil series mapped on public lands were identified using published soil surveys, advance soil sheets, land type surveys, and a Michigan County map atlas (MDNR, 1984). For each series, six counties were randomly and independently

selected with one pedon to be located and sampled in each county. Within each county selected, soil sheets that contained map units of the desired soil series on public lands were identified and randomly ordered. Within a selected soil sheet, map units were assigned random numbers which determined the order in which they were visited and evaluated for sampling.

Sampling sites were selected during field checks to confirm that: 1) the location was forested, 2) the existing stand was 40 years old or older (determined by increment cores from one or more dominant or co-dominant trees), 3) there was no evidence of recent major soil disturbance, and 4) bucket auger borings indicated that the soil profile was within the range of morphological characteristics for the target series given in SCS soil description and interpretation sheets (SCS-USDA). No subjective attempt was made to include or avoid pedons exhibiting extreme morphological characteristics. At the first point a criterion was not satisfied, the location would be rejected. The next map unit in random order on the same soil sheet would then be located and its acceptability evaluated as above. If all potential sampling locations on a soil sheet were rejected, the map units on successive randomly selected soil sheets would be similarly evaluated until a sampling location was accepted.

After independent selection of the six county locations for each series, but prior to initiation of fieldwork,

counties were grouped geographically so that one pedon of each series would be included in each of six sampling blocks. This incorporated a randomized complete block design into field sampling (Figure 4.1). Geographic sampling blocks allowed for efficient use of travel time and sampling effort, as well as removing from error any effects related to season of sampling, changes in sampling technique over time, regional differences in SO_4-S deposition, and day-to-day laboratory analytical variations. The two mesic zone pedons and the four frigid zone pedons included in each block did not have geographic similarities (Figure 4.1), but were similar in terms of time of sampling and laboratory analysis. The basic analysis of variance structure for inter-series comparisons takes the following form:

Source	Degrees of Freedom
Block	5
Series	5
Error	25
Total	35

FIELD SAMPLING METHODS

The pit sampling procedure employed was adapted from USDA (1982), Ellis et al. (1976), and Heilman (1971). Within the selected map unit, soil pit locations were subjectively located away from roads, fence rows, windthrow areas, skid trails, animal burrows, or other obvious features that might cause deviation from normal stand or

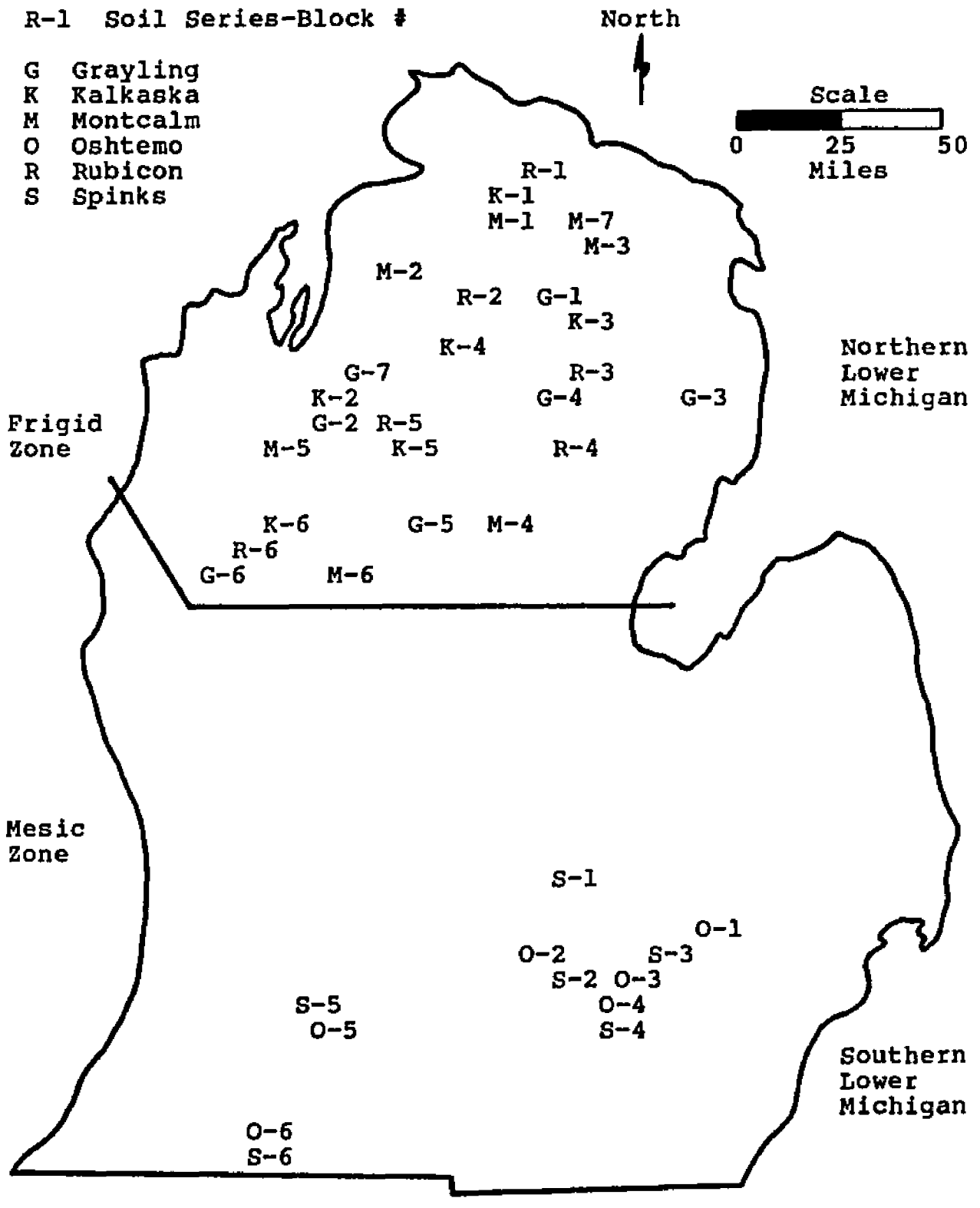

Figure 4.1

Locations and Block Assignments
of Sampled Pedons

soil conditions. Pits were approximately 1 by 2 meters across and excavated to at least 160 cm deep, or into the C horizon, whichever was deeper. Soil profiles were described following standard soil survey procedures. Horizon thicknesses were measured along three vertical transects on the pit face and averaged. Two 25 cm^3 bulk density samples were taken from each horizon with an Eley volumeter (Soiltest, 1971) and placed in soil moisture cans. Starting with the C horizon and proceeding upwards, each horizon was sampled in a vertical pattern 30 to 50 cm wide, using loose samples representing the entire cross section of the horizon. Samples were placed in plastic coated paper containers for transportation to the laboratory.

Upon completion of description and sampling, soil pits were filled in, leveled, and topsoil and leaf litter replaced to return the site to its approximate original condition. Thirty-six pedons meeting series descriptions were located and sampled between June and September of 1985. Two pedons that were found not to meet desired specifications after soil pit excavation ("Block 7") were also sampled. Locations of sampled pedons are shown in Figure 4.1. Brief composite descriptions of each series, derived from the profile descriptions of sampled pedons, are presented below. Soil profile descriptions for individual pedons are contained in Appendix B.

GRAYLING (mixed, frigid Typic Udipsamments)

A/E	0-6 cm	Black (N 2/0) sand (5-7 cm thick)
Bw1	6-23 cm	Dark brown (7.5YR 4/4) sand (15-21 cm thick)
Bw2	23-48 cm	Strong brown (7.5YR 4/6) sand (19-33 cm thick)
BC	48-89 cm	Yellowish brown (10YR 5/4) sand (30-49 cm thick)
C	89-167 cm	Light yellowish brown (10YR 6/4) sand

RUBICON (sandy, mixed, frigid Entic Haplorthods)

A	0-4 cm	Black (10YR 2/1) sand to loamy sand (3-6 cm thick)
E	4-12 cm	Light brownish gray (10YR 6/2) sand to loamy sand (5-11 cm thick)
Bs1	12-34 cm	Strong brown (7.5YR 4/6) sand (16-30 cm thick)
Bs2	34-58 cm	Strong brown (7.5YR 5/6) sand (18-33 cm thick)
BC	58-111 cm	Light yellowish brown (10YR 6/4) sand (28-69 cm thick)
C	111-175 cm	Light yellowish brown (10YR 6/4) sand

KALKASKA (sandy, mixed, frigid Typic Haplorthods)

A	0-5 cm	Black (10YR 2/1) sand to loamy sand (0-5 cm thick)
E	5-23 cm	Grayish brown (10YR 5/2) sand to loamy sand (10-27 cm thick)
Bh1	23-41 cm	Dark reddish brown (5YR 3/2) sand to loamy sand (10-23 cm thick)
Bh2	41-67 cm	Dark brown (7.5YR 3/4) sand to loamy sand (0-43 cm thick)
Bs	67-96 cm	Strong brown (7.5YR 4/6) sand to loamy sand (19-42 cm thick)
BC	96-149 cm	Yellowish brown (10YR 5/4) sand to loamy sand (32-71 cm thick)
C	149-189 cm	Light yellowish brown (10YR 6/4) sand to loamy sand

MONTCALM (coarse-loamy, mixed, frigid Eutric Glossoboralfs)

A	0-8 cm	Black (10YR 2/1) loamy sand (0-13 cm thick)
E	8-19 cm	Dark grayish brown (10YR 4/2) loamy sand (0-20 cm thick)
Bh	19-46 cm	Dark brown (7.5YR 3/4) loamy sand (15-45 cm thick)
Bs	46-80 cm	Dark brown (7.5YR 4/4) loamy sand (0-58 cm thick)
E'	80-113 cm	Yellowish brown (10YR 5/4) sand to loamy sand (13-53 cm thick)
E'2 & Bt	113-221 cm	Pale brown (10YR 6/3) sand to loamy sand (E'2) with bands, layers and lenses of reddish brown (5YR 4/4) sandy loam to sandy clay loam (Bt) (E'2 0-96 cm thick, Bt 18-49 cm thick)
C	221-261 cm	Light Brown (7.5YR 6/4) sand to loamy sand

OSHTEMO (coarse-loamy, mixed, mesic Typic Hapludalfs)

A	0-13 cm	Very dark grayish brown (10YR 3/2) loamy sand to sandy loam (9-20 cm thick)
E	13-64 cm	Dark yellowish brown (10YR 4/4) loamy sand to sandy loam (35-70 cm thick)
Bt1	64-86 cm	Strong brown (7.5YR 4/6) sandy loam (14-33 cm thick)
Bt2	86-124 cm	Strong brown (7.5YR 4/6) sandy loam (21-58 cm thick)
BC	124-164 cm	Dark yellowish brown (10YR 4/4) loamy sand (0-62 cm thick)
2C	164-222 cm	Yellowish brown (10YR 5/4) sand and gravel

SPINKS (sandy, mixed, mesic Psammentic Hapludalfs)

A	0-11 cm	Very dark grayish brown (10YR 3/2) loamy sand (4-20 cm thick)
E1	11-45 cm	Yellowish brown (10YR 5/6) loamy sand (26-40 cm thick)
E2	45-78 cm	Yellowish brown (10YR 5/4) sand to loamy sand (20-45 cm thick)
E' & Bt	78-221 cm	Yellowish brown (10YR 5/4) sand to loamy sand (E') with bands and lamellae of dark brown (7.5YR 4/4) sandy loam (Bt) (E' 45-174 cm thick, Bt 24-79 cm thick)
C	221-255 cm	Yellowish brown (10YR 5/4) sand to loamy sand

LABORATORY AND ANALYTICAL METHODS

On return to the laboratory, soil samples were air-dried at 25 ^{o}C, passed through a 2 mm sieve, and stored in plastic coated paper containers prior to analysis. Air-dry moisture content (θ_m) of samples was determined by weighing an exact quantity (target weight 10.0 g) of soil to 0.001 g, drying the sample at 105 ^{o}C for 24 hours, and re-weighing. θ_m was calculated as a decimal fraction of oven-dry soil weight. All analyses were performed using air-dry samples. Resulting analytical values were corrected to an oven-dry weight basis using $1 + \theta_m$; air-dry weight divided by $1 + \theta_m$ equalling oven-dry weight. Bulk density samples were oven-dried at 105 ^{o}C for 24 hours, cooled in a dessicator, and weighed to 0.001 g. Bulk density (g cm^{-3}) was calculated based on oven-dry weight of the 50 cm^3 sample.

Based on the results of preliminary sulfate adsorption studies (Chapter III), a relative measure of adsorption was determined by equilibrating air-dry soil samples in solutions containing 10 mg S L^{-1}. The sulfate concentration employed was selected to reduce discrepancies related to air-drying noted at higher sulfate concentrations, and to approximate soil solution sulfate concentrations under field conditions. The 10.0 gram samples were shaken for 24 hours in 50 mL of 0.01 M $CaCl_2$ containing sulfate added as Na_2SO_4. Soluble organic matter was removed by shaking samples for an additional 30 minutes with 0.2 g of HCl-washed activated charcoal. Solutions were filtered through Whatman # 42

filter paper and the filtrate was analyzed for SO_4-S by automated $BaSO_4$ turbidimetry (Wall et al., 1980). Sulfate adsorbed (mg S kg^{-1}) was calculated from the disappearance of sulfate from solution.

Initial levels of extractable SO_4-S in soils were determined by shaking 20.0 g of soil and 0.4 g HCl-washed activated charcoal with 50 mL $Ca(H_2PO_4)_2.H_2O$ solution (500 mg P L^{-1}) for 30 minutes (Eik, 1980). Soil extracts were filtered through Whatman # 42 filter paper and analyzed for SO_4-S by automated $BaSO_4$ turbidimetry (Wall et al., 1980). Preliminary tests showed that addition of activated charcoal to both SO_4-S adsorption solutions and soil extracts was necessary to prevent interference from organic matter causing overestimation of SO_4-S concentrations, especially for A, E, and upper B horizon samples.

Separate dithionite-citrate, ammonium oxalate, and sodium pyrophosphate extractions for Fe and Al were performed for each sample following methods described in USDA (1972; 1982) and Olson and Ellis (1982). In all three procedures, 2.0 g soil samples were placed in 250 mL polyethylene bottles, a measured volume of extractant was added, and the sealed bottles were shaken on an oscillating shaker table at 160 opm for the recommended time (16 hours for dithionite-citrate and sodium pyrophosphate, 4 hours for ammonium oxalate). A preliminary study indicated that the amount of Fe and Al extracted did not differ between samples shaken on oscillating or reciprocating shaker tables. At

the end of the shaking period, Superfloc (five drops of 0.2% solution for dithionite-citrate; ten drops 0.4% solution for ammonium-oxalate and Na pyrophosphate) was added to samples, which were re-shaken for 30 seconds and allowed to settle for one hour. After settling, 45 mL of supernatant were decanted into 50 mL polypropylene centrifuge tubes and centrifuged for 15 minutes. Centrifuged samples were refrigerated until analyzed for Fe and Al by D-C argon plasma atomic emission spectrometry. Dithionite-citrate and Na pyrophosphate extracts were analyzed without dilution. Ammonium oxalate extracts were diluted by 1/2 with 0.58 M LiCl solution, to give a sample concentration of 2000 mg Li^{+} L^{-1} to enhance analytical sensitivity. Dithionite-citrate extracts organically bound, inorganic amorphous, and crystalline Fe. Ammonium oxalate extracts organically bound and inorganic amorphous Fe. Sodium pyrophosphate extracts organically bound Fe. Al fractions extracted are less specific and more overlap exists.

Exchangeable Al^{3+} was determined by shaking samples in 50 mL of 1 M KCl for 30 minutes (Barnhisel and Bertsch, 1982). Sample size was 5.0 g for A, E, Bw, Bs, Bh, and Bt horizons and 10.0 g for BC, E', and C horizons. Solutions were filtered through Whatman # 42 filter paper and then diluted by 1/5 with deionized water to reduce salt concentration prior to analysis by D-C argon plasma atomic emission spectrometry. Exchangeable cations were extracted by shaking 10.0 g samples for 30 minutes with pH 7.0 1 M

ammonium acetate (USDA, 1972; 1982; Thomas, 1982). Extracts were filtered through Whatman # 42 filter paper and stored in polyethylene bottles under refrigeration prior to analysis for Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+} by D-C argon plasma atomic emission spectrometry. Effective cation exchange capacity was calculated as the sum of Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, and Al^{3+} on the basis of cmol (+) kg^{-1} (USDA, 1972). For the soils collected in this study, such calculations do not reflect true CEC's in horizons containing significant quantities of carbonates.

Extractable P was determined using a method based on that given by Olsen and Sommers (1982). 2.0 g soil and 12 mL Bray # 1 extracting solution (0.03 M NH_4F + 0.025 M HCl) were placed in 15 mL polystyrene centrifuge tubes, shaken for 10 minutes on a reciprocating shaker, and centrifuged for 10 minutes. 3.0 mL of supernatant were pipetted into autoanalyzer sample cups which were capped and refrigerated until colorimetrically analyzed for P by autoanalyzer (Technicon, 1977). Soil samples with pH values $\geq$ 6.5 were re-extracted using 0.5 g soil and 15 mL extractant, a higher solution:soil ratio being recommended (Smith et al., 1957) for samples containing carbonates.

Percent organic carbon was determined using the Walkley-Black method of H_2SO_4-$K_2Cr_2O_7$ oxidation followed by titration with 0.5 M $FeSO_4.7H_2O$ (USDA, 1972; Nelson and Sommers, 1982). Sample sizes were 0.5 to 1.0 g for A horizons, 2.0 g for E, Bh, Bs, and Bw horizons, and 5.0 to

10.0 g for E', Bt, BC, and C horizons.

Soil pH in water and in 0.01 M $CaCl_2$ was determined following a method given in USDA (1972). A Corning 125 pH meter equipped with separate glass pH and calomel reference electrodes was used to make pH measurements. For pH in water, 20.0 g soil and 20 mL deionized water were placed in a 100 mL polypropylene beaker and stirred three times over the next 30 minutes. After a 30 minute settling period, pH was measured with the pH electrode placed within the partly settled suspension and the reference electrode placed above in the clear supernatant. 20 mL 0.02 M $CaCl_2$ were then added to the soil suspension, resulting in a 1:2 soil:0.01 M $CaCl_2$ suspension. Samples were stirred twice at 15 minute intervals, and allowed to settle for 30 minutes before taking the second pH reading. Preliminary laboratory tests confirmed that this method gave $CaCl_2$ pH readings equivalent to those obtained using fresh 20.0 g soil samples to which 40 mL of 0.01 M $CaCl_2$ were added.

Particle size analysis was performed on E, Bt, E', BC, and C horizon samples from Spinks and Oshtemo series pedons. The hydrometer method described by Bouyoucos (1951) was employed, with modifications taken from Day (1965). A sample size of 100.0 g was used for samples classed as sands by field methods, and 50.0 g for samples classed as loamy sands or finer. Samples were pre-treated with H_2O_2 to remove organic matter (USDA, 1982) and mechanically dispersed in distilled water after the addition of 100 mL of

a pH 8.3 dispersing solution containing 45 g $(NaPO_3)_6$ and 5 g Na_2CO_3 L^{-1} (Day, 1965). Samples were transferred to sedimentation cylinders, brought to volume with distilled water, and placed in a water bath to allow temperature to equilibrate (21 ^oC) before taking the appropriate hydrometer readings. One cylinder containing only 100 mL dispersing solution and distilled water was included in each set to provide blank readings to adjust hydrometer readings.

Soil analyses were conducted in six blocks, corresponding to the sampling blocks described previously. Samples were independently randomized within blocks for each analytical procedure. With the exception of sulfate adsorption, extractable Al^{3+}, and particle size analyses, each analytical block consisted of 48 samples, including two bulk samples, two blank samples, and approximately 15% replication. Sulfate adsorption equilibrations were performed in blocks of 80 samples, allowing 100% replication and inclusion of two 10 mg S L^{-1} standards, two bulk samples, and two blank samples (0.01 M $CaCl_2$) per block. Exchangeable Al^{3+} extractions were conducted without replication in 80-sample lots, including two sample blocks, one bulk sample, and two blank samples per lot. Particle size analyses were conducted in blocks of 12, including one blank sample per block. Results of all analyses were corrected for blank sample values. Analytical data for individual pedons are presented in Appendix B. Values reported are based on mathematical calculations using

concentrations in extractant solutions and appropriate dilution factors. Absolute precision of reported values is not implied nor should it be inferred. Precision estimates for analyses can be made by examining the variability of bulk sample data (Appendix C). Average coefficients of variation of replicate samples (not presented) were very similar to those found for bulk samples.

METHODS OF STATISTICAL ANALYSIS

Data manipulations and statistical calculations were performed using Microstat (Ecosoft, 1984) and NCSS (Hintze, 1985), two microcomputer statistical software packages. Where appropriate, logarithmic transformations were applied to data to approximate normality and create homogeneity of variance. Mean separation for analysis of variance results was accomplished using Tukey's w procedure (Steel and Torrie, 1980). Significance was judged at a probability level of 0.05. Correlation analyses were performed on untransformed data. Regression analyses were performed on logarithmically transformed data using ordinary least squares procedures. Examination of residuals followed procedures and recommendations discussed in Draper and Smith (1980), Chatterjee and Price (1977), Seber (1977), and Mosteller and Tukey (1977). Linear discriminant analysis followed procedures similar to those described by Morrison (1976). Further details on methods of statistical analysis for specific analyses are contained in subsequent chapters.

Chapter V

SULFATE ADSORPTION AND EXTRACTABLE SULFATE IN MICHIGAN FOREST SOILS

The primary objectives of this portion of the study were to determine the ability of selected Michigan forest soils to adsorb sulfate under laboratory conditions, and to determine initial levels of extractable sulfate present. The six soil series studied were the Grayling, Rubicon, Kalkaska, Montcalm, Spinks, and Oshtemo, with six pedons of each series sampled as described in Chapter IV. This chapter will discuss sulfate adsorption and extractable sulfate by horizon for the series studied. Inter-series comparisons of sulfate adsorption and extractable sulfate are presented and examined. Extractable sulfate contents of pedons grouped by series and geographic region are briefly discussed. Significance of results to acid deposition effects include identification of sulfate adsorbing soil horizons and comparisons of relative sulfate adsorption abilities between soil series, both aspects pertinent to classification of soil sensitivity to effects of acid deposition.

Data for Oshtemo E1 and E2 (2 pedons), Oshtemo Bt2 and Bt3 (1 pedon), Kalkaska Bh1 and Bh2 (3 pedons), and Montcalm Bh and Bs (4 pedons) horizons were combined within pedons using weighted averages for within-series analyses of

variance of sulfate adsorption and extractable sulfate. Preliminary analyses of variance indicated that the subdivided horizons did not differ significantly in either sulfate adsorption or extractable sulfate. For within series comparisons, logarithmic transformations were applied to sulfate adsorption data [(+,-) $\ln(|\text{mg S kg}^{-1}|+1)$] and to extractable SO_4-S data {$\ln[(\text{mg S kg}^{-1})+1]$} prior to statistical analysis to establish homogeneity of variance.

One Spinks pedon sampled (Block I, Appendix B) had high levels of extractable sulfate in the Bt (11.6 mg S kg^{-1}) and C (29.9 mg S kg^{-1}) horizons. Both horizons also released high amounts of sulfate (Bt = 6.1 mg S kg^{-1}; C = 36.7 mg S kg^{-1}) during adsorption equilibrations. Compared to the Bt and C horizons of other Spinks pedons, this was anomalous behavior. In other pedons, Bt horizons adsorbed sulfate, while C horizons weakly adsorbed or released small quantities of sulfate (Appendix B). For this reason, data from Bt and C horizons of this pedon were excluded from sulfate adsorption analyses of variance, and C horizon data were excluded from extractable sulfate analyses of variance.

This Spinks pedon was situated downwind from a large urban area (Lansing, Michigan), and the high amounts of sulfate in Bt and C horizons apparently indicate high sulfate deposition from this source, with subsequent translocation to and accumulation in Bt and C horizons. Williams and Steinbergs (1962) found that sulfate could be co-precipitated from solution with $CaCO_3$, and that

appreciable amounts of sulfate could be extracted from calcareous subsoils with 0.15% $CaCl_2$. The high levels of extractable sulfate present in the calcareous C horizon of this Spinks pedon may be evidence of such co-precipitation. High release of sulfate from these horizons during adsorption equilibrations was related to the effects of air-drying on sulfate release, along with extraction by the 0.01 M $CaCl_2$ used as a supporting electrolyte.

SULFATE ADSORBING HORIZONS

Separate analyses of variance (Appendix D, Table D.3) conducted for each series indicated that soil horizons differed in ability to adsorb sulfate (Figures 5.1 to 5.6). The A horizons of all series released SO_4-S during laboratory equilibration, related to high organic carbon content (Table 5.1) and weak anion retention in surface soils (Ensminger, 1954; Johnson and Todd, 1983; Singh, 1984b; Evans, 1986). Sulfate release by surface horizons was encouraged by air-drying of samples and by equilibration in 0.01 M $CaCl_2$, which will extract soluble and weakly adsorbed sulfate from acid surface soils (Williams and Steinbergs, 1962). Under field conditions, surface horizons of forest soils may be important locations of sulfate retention through microbial immobilization of sulfate as organic S (Fitzgerald and Strickland, 1982; David et al., 1983; Swank et al., 1984; Schindler et al., 1986). E horizons of the Rubicon (Figure 5.2), Kalkaska (Figure 5.3),

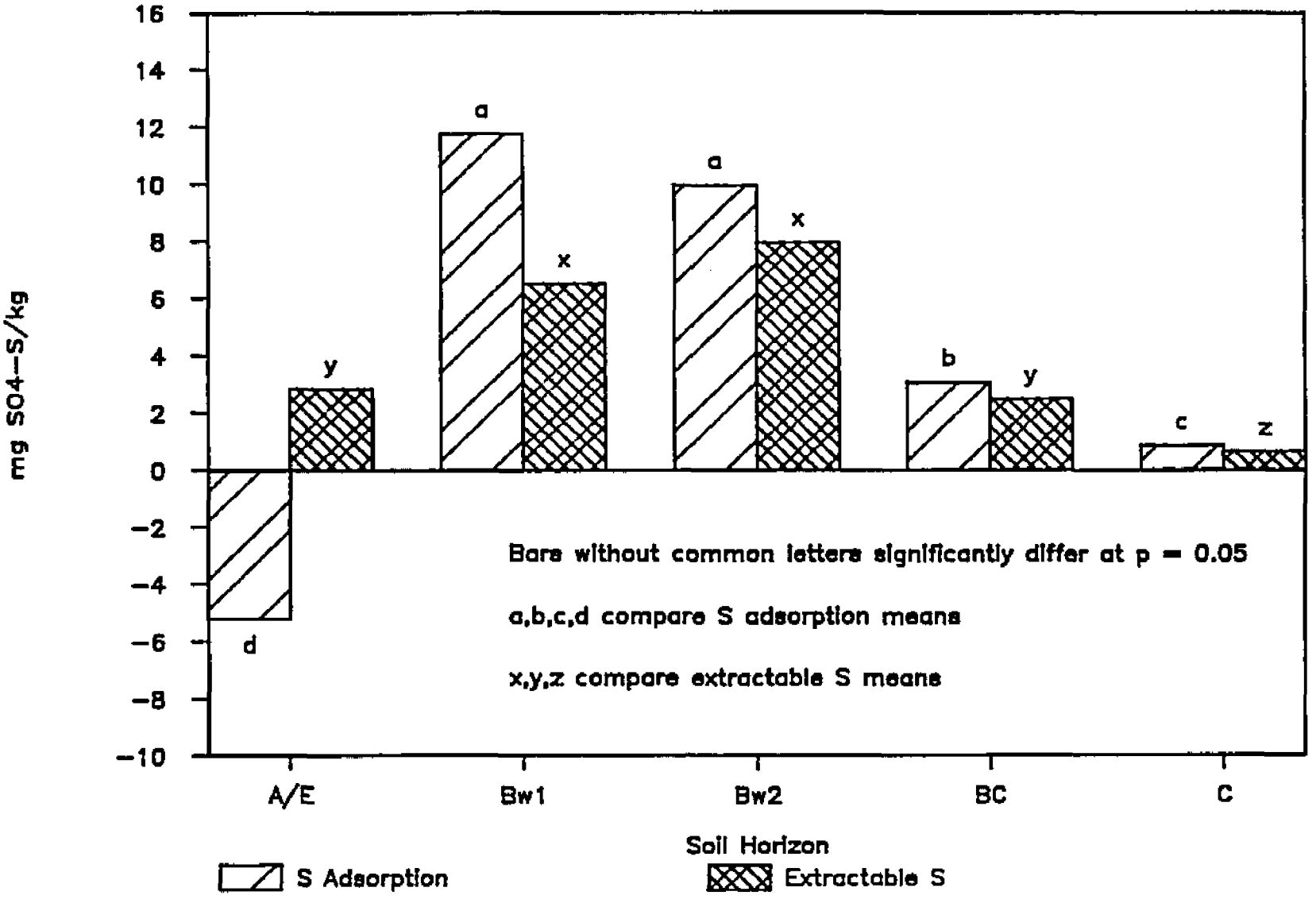

Figure 5.1

S Adsorption and Extractable S in the Grayling Series

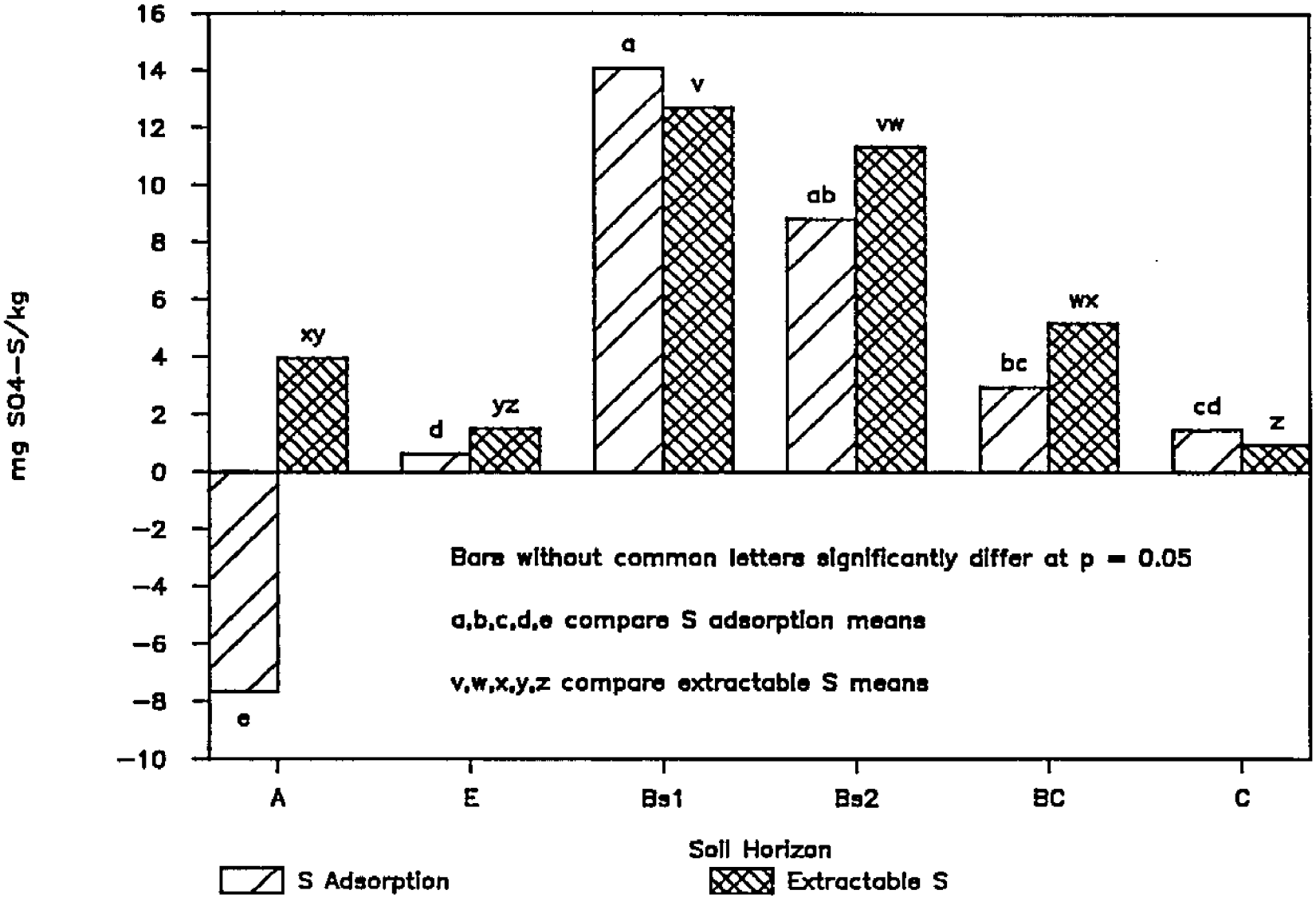

Figure 5.2

S Adsorption and Extractable S in the Rubicon Series

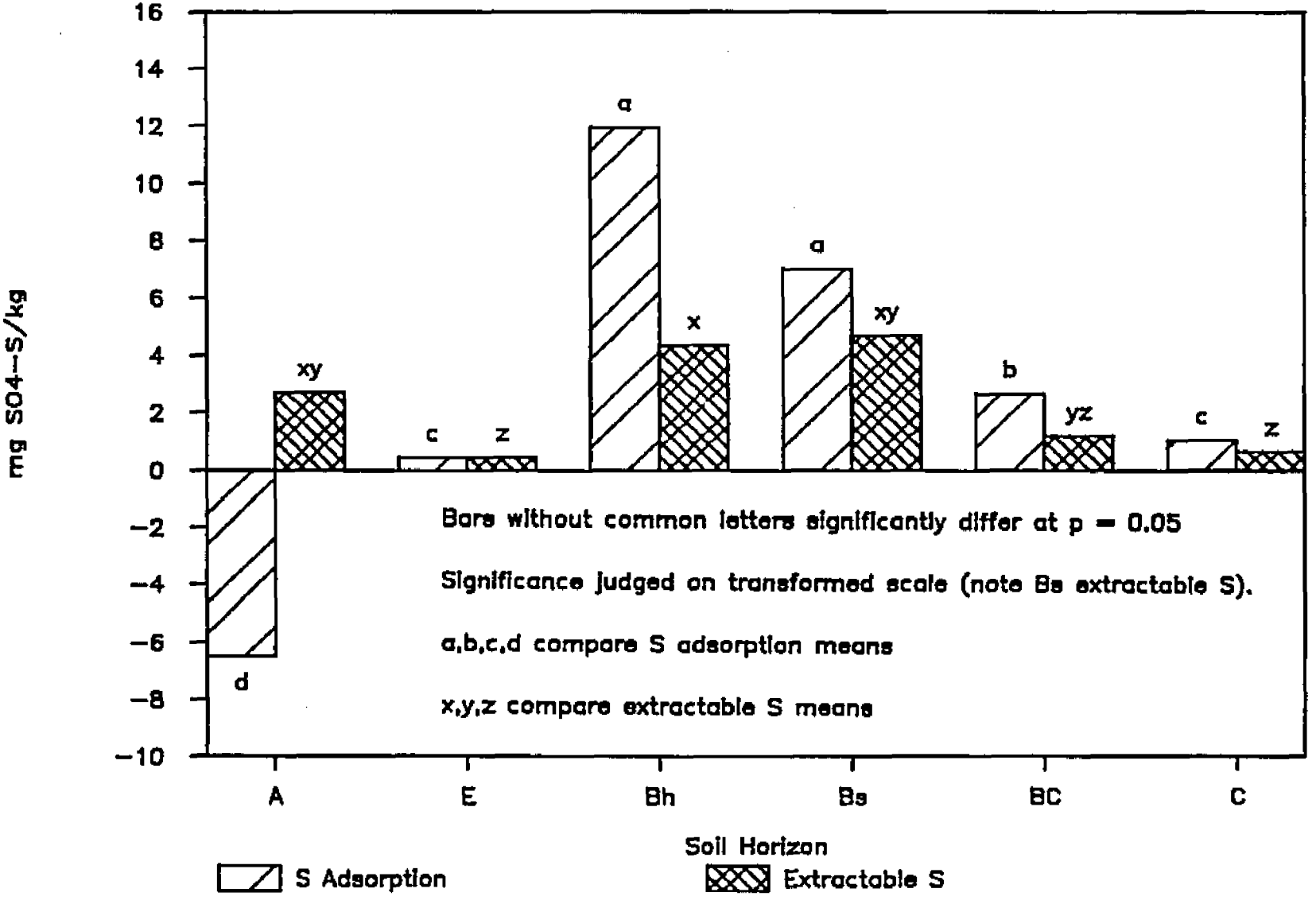

Figure 5.3

S Adsorption and Extractable S in the Kalkaska Series

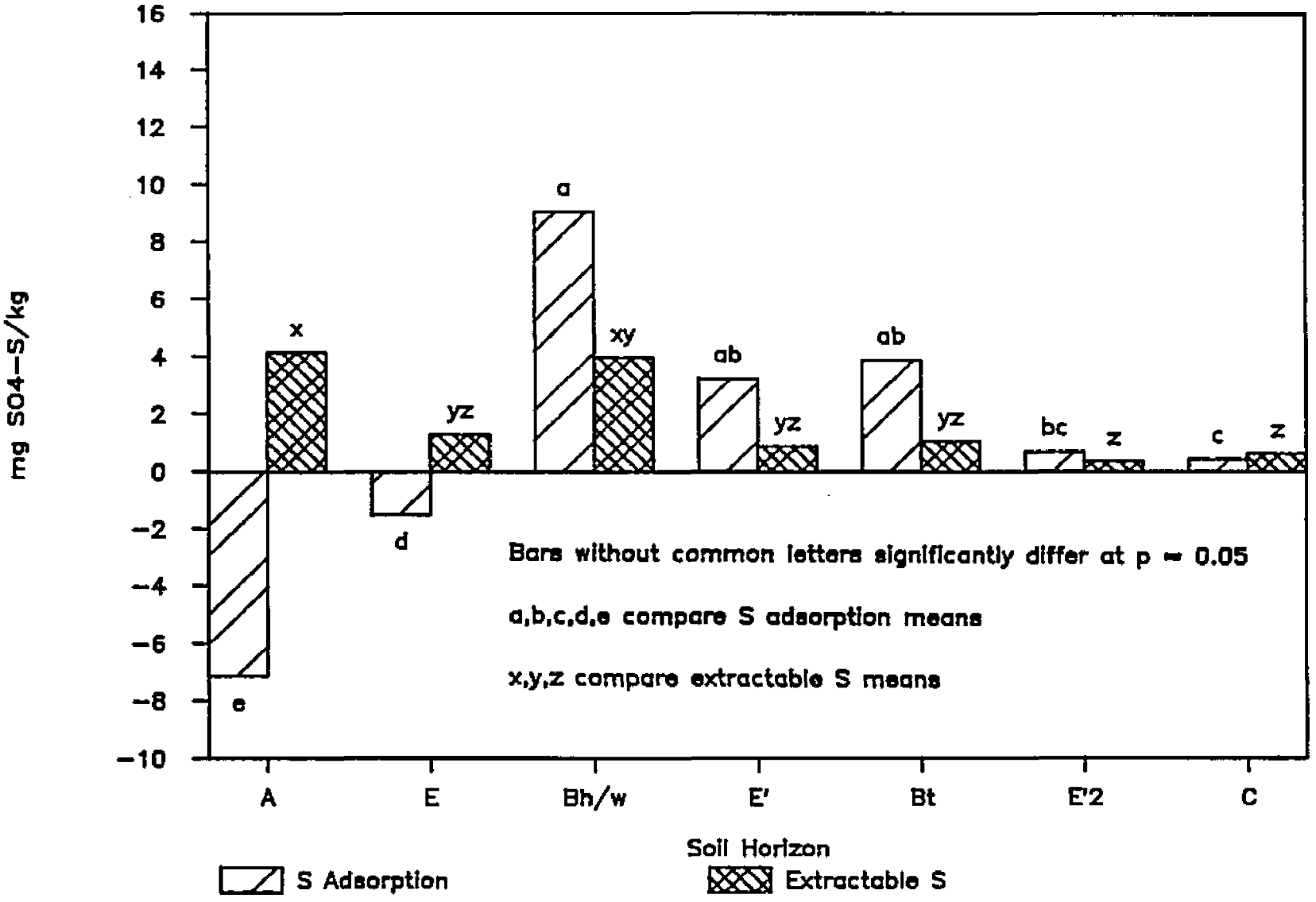

Figure 5.4

S Adsorption and Extractable S in the Montcalm Series

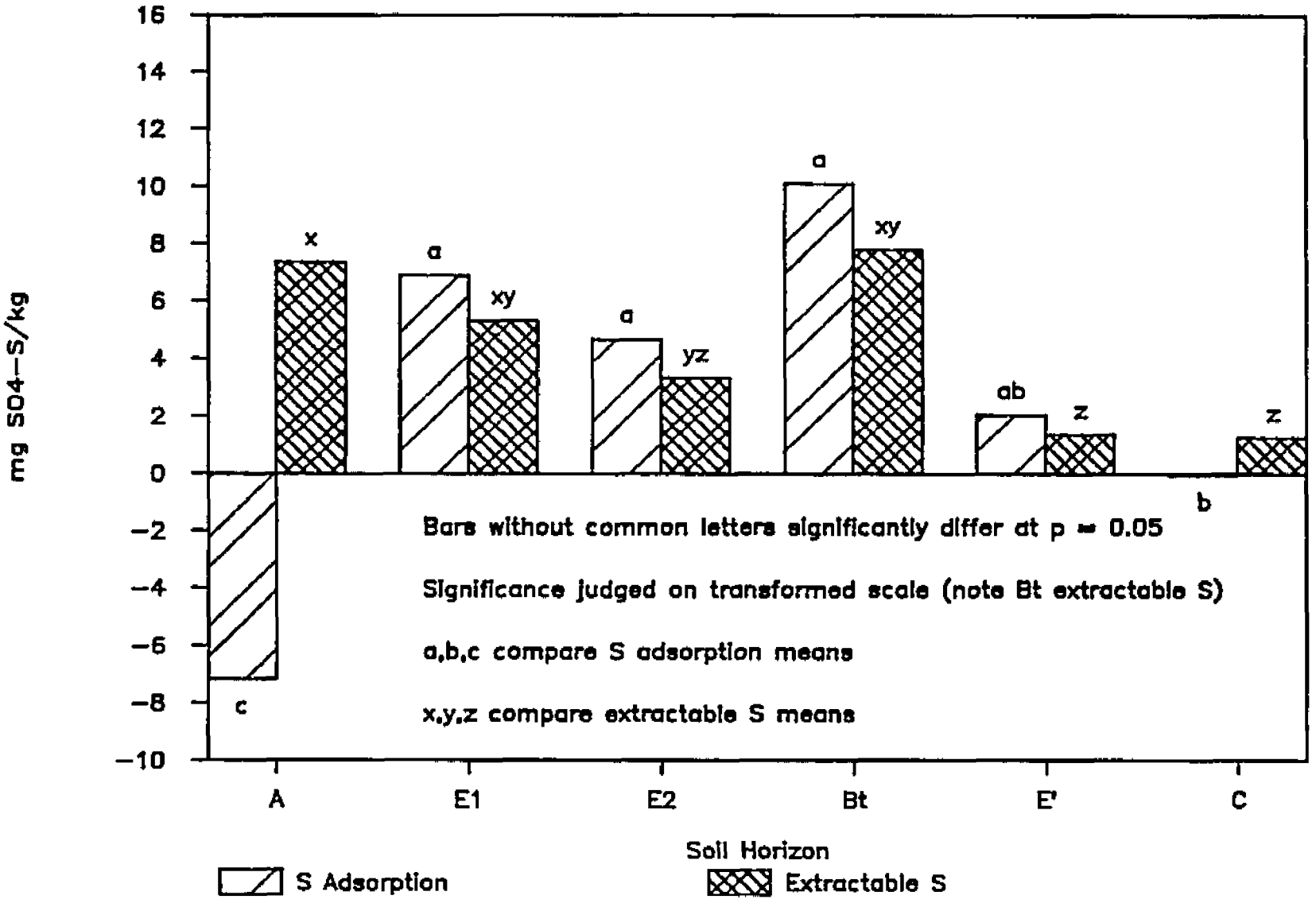

Figure 5.5

S Adsorption and Extractable S in the Spinks Series

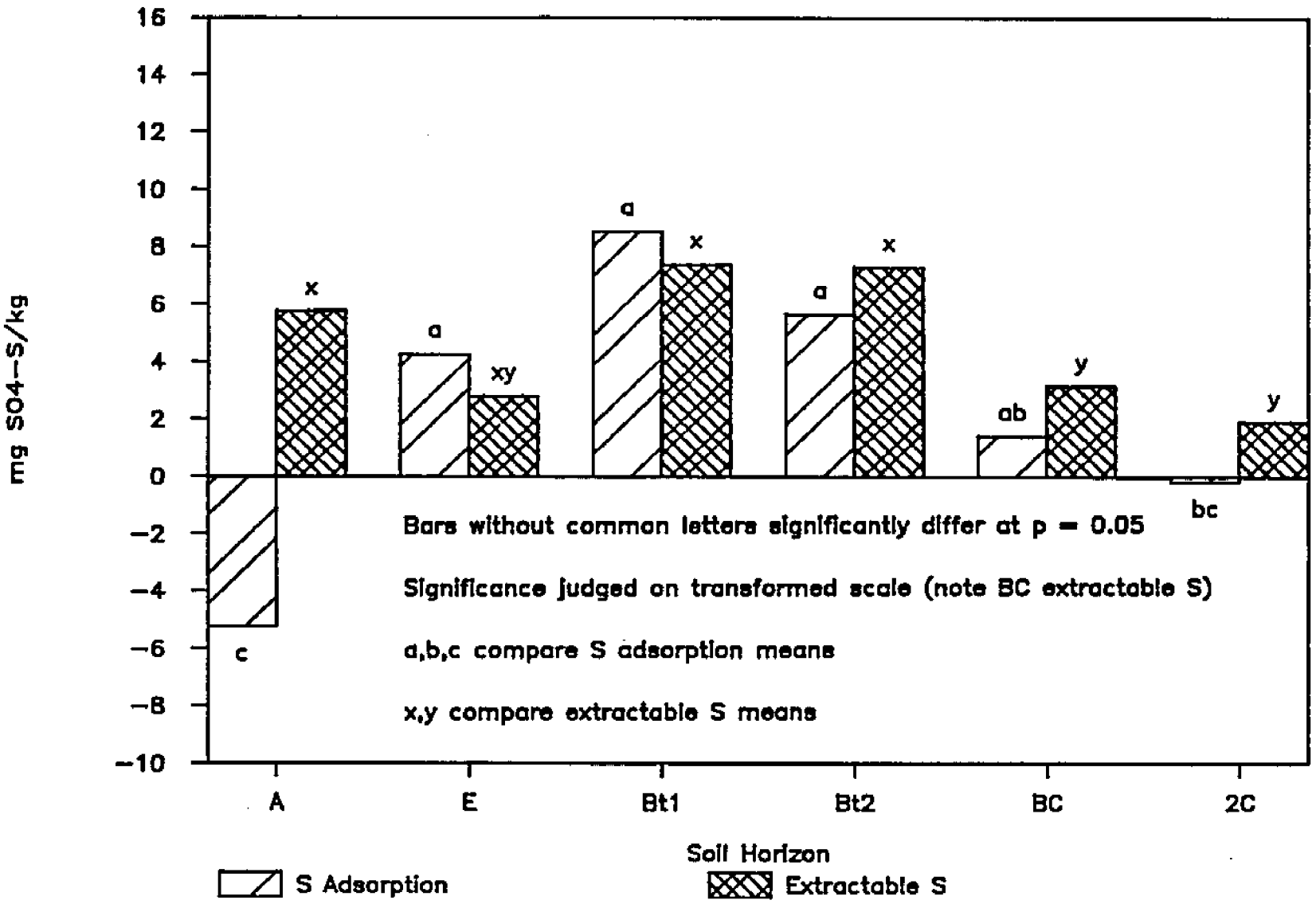

Figure 5.6

S Adsorption and Extractable S in the Oshtemo Series

Table 5.1

Selected Soil Chemical Properties by Series

Grayling

Soil[1] Hor.	pH-H_2O[2] Mean[†]	SD	% Org. C[3] Mean	SD	% Bases[4] Mean	SD	AO-Al[5] Mean	SD	DC-Fe[6] Mean	SD
A/E	4.52	0.36	3.19	0.56	63.0	29.9	0.8	0.2	2.1	0.5
Bw1	5.29	0.40	0.49	0.11	38.1	27.3	1.7	0.4	3.0	0.5
Bw2	5.28	0.29	0.23	0.05	28.8	14.8	1.5	0.2	2.3	0.3
BC	5.45	0.35	0.06	0.01	39.1	17.0	0.7	0.2	1.0	0.5
C	6.06	0.51	0.03	0.01	74.9	28.3	0.2	0.1	0.7	0.2

Rubicon

Soil Hor.	pH-H_2O Mean	SD	% Org. C Mean	SD	% Bases Mean	SD	AO-Al Mean	SD	DC-Fe Mean	SD
A	4.08	0.26	2.55	0.40	62.3	21.0	0.3	0.1	1.1	0.2
E	4.30	0.23	0.56	0.30	29.3	14.8	0.2	0.1	0.9	0.4
Bs1	5.08	0.15	0.49	0.07	18.5	8.3	2.6	0.8	2.8	0.5
Bs2	5.19	0.25	0.19	0.07	24.7	15.8	1.8	0.7	1.6	0.4
BC	5.34	0.30	0.05	0.03	35.1	15.4	0.8	0.3	0.9	0.4
C	5.73	0.49	0.02	0.01	51.3	27.9	0.4	0.2	0.6	0.2

Kalkaska

Soil Hor.	pH-H_2O Mean	SD	% Org. C Mean	SD	% Bases Mean	SD	AO-Al Mean	SD	DC-Fe Mean	SD
A	4.48	0.50	2.49	0.13	83.6	12.8	0.3	0.2	1.4	0.3
E	4.48	0.31	0.38	0.17	41.8	12.0	0.2	0.1	1.0	0.4
Bh1	5.46	0.37	0.69	0.17	56.7	29.4	2.6	1.4	3.6	0.9
Bh2	5.53	0.33	0.46	0.06	45.1	18.2	2.4	0.2	2.2	0.3
Bs	5.56	0.41	0.22	0.07	46.1	24.2	1.6	0.9	1.6	0.3
BC	5.69	0.38	0.08	0.04	54.4	26.4	0.6	0.3	1.0	0.3
C	5.89	0.47	0.04	0.02	67.2	33.4	0.3	0.2	0.7	0.1

† n = 6 pedons for Rubicon, Kalkaska, Spinks, and Oshtemo
n = 7 pedons for Grayling and Montcalm
SD = 1 Standard Deviation

1 Soil Horizon
2 pH measured in H_2O, $-Log(H^+)$
3 % organic carbon
4 % base saturation, % of effective CEC
5 Ammonium oxalate extractable Al, g Al kg^{-1}
6 Dithionite-citrate extractable Fe, g Fe kg^{-1}

Table 5.1 (continued)

Montcalm

Soil[1] Hor.	pH-H_2O[2] Mean[†]	SD	% Org. C[3] Mean	SD	% Bases[4] Mean	SD	AO-Al[5] Mean	SD	DC-Fe[6] Mean	SD
A	5.02	0.36	3.14	1.38	96.9	3.9	0.5	0.2	2.3	1.4
E	4.41	0.29	0.84	0.50	57.2	23.7	0.2	0.1	1.2	0.3
Bh	5.25	0.29	0.77	0.55	46.2	23.5	2.0	1.5	3.8	1.1
Bs	5.39	0.19	0.43	0.26	33.0	15.7	2.3	0.9	2.5	0.5
E'	5.85	0.36	0.10	0.09	67.5	20.5	0.6	0.4	1.7	0.4
Bt	6.78	0.90	0.12	0.06	95.7	10.4	0.9	0.4	4.4	1.2
E'2	6.90	1.22	0.03	0.02	94.4	7.3	0.1	0.0	1.1	0.5
C	8.34	0.95	0.07	0.07	98.7	3.5	0.3	0.3	1.8	1.3

Spinks

Soil Hor.	pH-H_2O Mean	SD	% Org. C Mean	SD	% Bases Mean	SD	AO-Al Mean	SD	DC-Fe Mean	SD
A	4.84	0.60	2.65	1.40	69.2	31.3	0.9	0.3	3.8	0.5
E1	4.97	0.29	0.27	0.15	30.8	17.8	0.9	0.2	3.9	1.0
E2	5.38	0.45	0.09	0.06	52.4	29.0	0.5	0.2	3.4	1.2
E'	5.98	0.20	0.05	0.03	91.2	9.9	0.3	0.1	3.4	1.2
Bt	6.02	0.59	0.08	0.03	98.0	1.7	0.7	0.2	8.6	3.0
C	8.27	0.89	0.05	0.04	100.0	0.0	0.1	0.0	2.9	1.3

Oshtemo

Soil Hor.	pH-H_2O Mean	SD	% Org. C Mean	SD	% Bases Mean	SD	AO-Al Mean	SD	DC-Fe Mean	SD
A	5.28	0.51	2.09	0.91	82.4	29.4	1.2	0.3	4.9	0.3
E	5.34	0.33	0.22	0.08	62.2	21.2	0.7	0.3	4.6	0.6
Bt1	5.68	0.78	0.10	0.04	84.1	26.8	0.7	0.2	8.8	2.2
Bt2	5.80	0.59	0.09	0.03	88.7	22.1	0.6	0.1	7.6	1.9
BC	6.53	0.96	0.05	0.02	97.8	3.0	0.3	0.0	4.1	1.3
2C	8.38	0.73	0.03	0.02	100.0	0.0	0.1	0.0	2.6	0.7

† n = 6 pedons for Rubicon, Kalkaska, Spinks, and Oshtemo
n = 7 pedons for Grayling and Montcalm
SD = 1 Standard Deviation

1 Soil Horizon
2 pH measured in H_2O, $-Log(H^+)$
3 % organic carbon
4 % base saturation, % of effective CEC
5 Ammonium oxalate extractable Al, g Al kg^{-1}
6 Dithionite-citrate extractable Fe, g Fe kg^{-1}

and Montcalm (Figure 5.4) series adsorbed sulfate weakly or released sulfate, while E horizons of the Spinks (Figure 5.5) and Oshtemo (Figure 5.6) series had stronger adsorption abilities. Increased sulfate adsorption in mesic E horizons was related to their higher Al and Fe and lower organic matter contents (Table 5.1).

In contrast to A horizons, illuvial horizons adsorbed sulfate during laboratory equilibration (Figures 5.1 to 5.6). In frigid zone series (Grayling, Rubicon, Kalkaska, and Montcalm), adsorption followed a similar pattern with upper Bw, Bs, and Bh horizons adsorbing significantly more SO_4-S than underlying BC, E'2, and C horizons. In mesic zone series (Spinks and Oshtemo), sulfate adsorption was highest in E and Bt horizons. Horizons with high sulfate adsorption abilities were high in Fe and Al, and had mean pH values of 6 or below (Table 5.1). Adsorption of sulfate in B horizons of forest soils has previously been reported by Singh (1980b), Johnson and Todd (1983), Fuller et al. (1985), and Weaver et al. (1985).

Reductions in solution sulfate concentration during equilibration with Bw, Bs, Bh, and Bt samples ranged from 1.0 to 3.9 mg S L^{-1}, suggesting that these horizons are relatively weak sulfate adsorbers, as reported for B horizons of Spodosols in the northeastern United States (Johnson and Todd, 1983). Retention of sulfate in field plots is usually greater than that predicted from laboratory adsorption studies (Johnson et al., 1979a; Johnson and

Henderson, 1979; Johnson, D.W., et al., 1981). In the present study, amounts of sulfate adsorbed by soils provide a relative index of adsorption ability, and probably underestimate amounts of sulfate that could be retained under field conditions. Relationships between soil properties and sulfate adsorption in these soils are discussed in Chapter VI.

EXTRACTABLE SULFATE

Within-series analyses of variance were conducted for extractable sulfate data (Appendix D, Table D.4). Levels of extractable SO_4-S comparable to those present in subsurface horizons were found in the A horizons of Kalkaska, Montcalm, Spinks, and Oshtemo series (Figures 5.3 to 5.6). Levels of extractable SO_4-S in A horizons of Grayling and Rubicon (Figures 5.1, 5.2) soils were significantly lower than extractable sulfate in Bw and Bs horizons. The latter SO_4-S distribution is typical of acid forest soils, and was similar to that observed in Norwegian forest soils (Singh, 1980b) and in northeastern United States Spodosols (David et al., 1982; Johnson and Todd, 1983). Extractable sulfate in A and E horizons may represent water soluble sulfate, as found in O and E horizons of Spodosols by Fuller et al. (1985), may be sulfate released from organic forms during air-drying (Freney, 1958; Barrow, 1961; Williams and Steinbergs, 1964; Tabatabai and Bremner, 1972; David et al., 1982), or may be sulfate weakly adsorbed to positively

charged organic colloids (Chao et al., 1962b). Soluble sulfate was low (2 to 68 mg S kg^{-1}) in the surface horizons of most well-drained soils examined by Williams and Steinbergs (1962), generally comprising less than 5% of total S. The majority of total S in surface horizons is contained in organic forms (Williams and Steinbergs, 1962; Singh, 1980b; David et al., 1982).

In frigid zone A, A/E, and E horizons, extractable SO_4-S was significantly ($P < 0.01$, $n = 37$) correlated ($r = 0.93$) with SO_4-S released during adsorption equilibration. This correlation suggests that in surface horizons, extractable S and desorbed S are both measures of the same SO_4-S pool, $CaCl_2$ being capable of extracting amounts of sulfate similar to those extracted by phosphate in acid surface soils (Williams and Steinbergs, 1962; 1964). Significant ($P < 0.01$) correlations were also present between sulfate desorption and organic carbon in frigid A, A/E, and E ($r = 0.79$, $n = 37$) and in mesic A ($r = 0.72$, $n = 12$) horizons, and between extractable SO_4-S and organic carbon ($r = 0.79$, $n = 37$) in frigid zone surface horizons. These correlations suggest that both extractable sulfate and sulfate desorbed during adsorption equilibrations reflect SO_4-S released either as a result of mineralization of organic S or by displacement of weakly adsorbed sulfate from protonated organic colloids by phosphate and chloride anions.

Extractable sulfate concentrations in subsurface horizons were high in those soil horizons with high sulfate

adsorption (Figures 5.1 to 5.6). Peaks of extractable sulfate in B horizons of other forest soils have been reported by Singh (1980b), Singh et al. (1980), David et al. (1982), Johnson and Todd (1983), and Fuller et al. (1985). Extractable SO_4-S was significantly ($P < 0.01$) correlated with SO_4-S adsorbed by B, E', and C horizons of frigid zone soils ($r = 0.57$, $n = 118$) and by E, B, and C horizons of mesic zone soils ($r = 0.68$, $n = 62$). Singh (1980b) found a comparable correlation ($r = 0.77$, $n = 17$) between S adsorbed and P extractable S in Norwegian forest soils. Since levels of extractable sulfate result from sulfate retention under ambient levels of deposition, these correlations suggest that laboratory sulfate adsorption is related to sulfate retention under field conditions. The positive correlation suggests that, on a regional scale, past sulfate deposition has not yet markedly impaired the ability of these soils to retain additional sulfate. In the present study, maximum extractable SO_4-S in B horizons of frigid zone soils ranged from 14 to 23 mg S kg^{-1}, compared to the 16 to 64 mg S kg^{-1} extracted from northeastern United States Spodosols by Fuller et al. (1985). This suggests Michigan Spodosols have not yet been as heavily impacted by sulfate deposition as similar soils in the Northeast.

SULFATE ADSORPTION - INTER-SERIES COMPARISONS

There were no significant differences in sulfate adsorption between series (Appendix D, Table D.5) when

compared on the basis of SO_4-S adsorbed in the upper 150 cm of sulfate adsorbing horizons (frigid zone A, A/E, E, and mesic zone A horizons excluded). Mean values, ranging from 9.6 g S m^{-2} for Grayling to 12.8 g S m^{-2} for Spinks, suggest that these soils have relatively low abilities to adsorb sulfate when compared to the annual SO_4-S wet deposition in Michigan of 0.6 to 0.9 g S m^{-2} (NADP, 1985a; 1985b; 1986).

An analysis of variance incorporating depth as a split plot factor (0-50, 50-100, 100-150 cm) in S-adsorbing horizons revealed a significant interaction between series and depth in the pedon (Table 5.2). Statistical analysis was performed on untransformed data, g S m^{-2}. The significant Series x Depth interaction is shown in Figure 5.7. Differences in sulfate adsorption between series were present when compared in 50 cm increments measured from the top of the uppermost sulfate adsorbing horizon. In the upper 50 cm, Rubicon adsorbed more SO_4-S than Oshtemo, largely a difference between the Rubicon Bs and the Oshtemo E horizons. The Rubicon Bs horizons were lower in pH and base saturation and higher in ammonium oxalate extractable Al than the Oshtemo E horizons (Table 5.1), a combination of properties that would account for higher S adsorption by Rubicon soils (Kamprath et al., 1956; Chao et al., 1963; Parfitt, 1982; Johnson and Todd, 1983; Fuller et al., 1985; Johnson et al., 1986). A trend of increasing adsorption from Grayling to Oshtemo is evident in the 50-100 cm depth, although no significant differences were present. In the

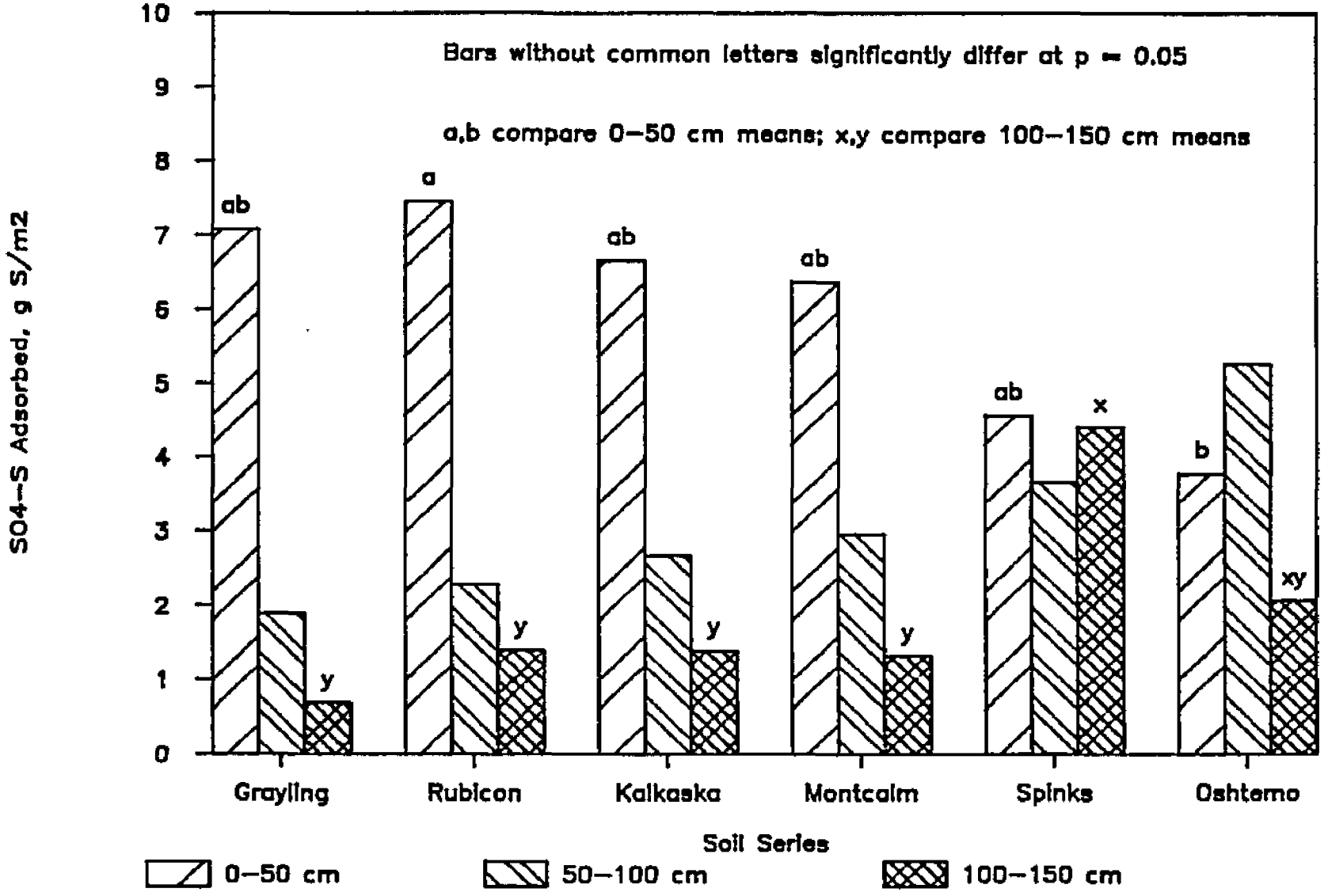

Figure 5.7

S Adsorption - Series x Depth Interaction

100-150 cm depth (Figure 5.7), Spinks had significantly higher SO_4-S adsorption than all four frigid zone series, reflecting the presence of Bt horizons high in clay and Fe in the solum of the Spinks series. The lower adsorption in Montcalm Bt horizons (Figure 5.4, 3.9 mg S kg^{-1}) as compared to higher adsorption in Spinks Bt horizons (Figure 5.5, 10.1 mg S kg^{-1}), may result from higher pH and lower Fe concentrations in Montcalm Bt horizons (Table 5.1).

Table 5.2

Analysis of Variance Results - Sulfate Adsorption

Source	DF	SS	MS	F	P
Block	5	64.2239	12.8448	1.76	0.16
Series	5	9.0549	1.8110	0.25	0.95
$Error_a$	25	181.8622	7.2745		
Depth	2	324.0440	162.0220	74.70	0.00
Series x Depth	10	147.2826	14.7283	6.79	0.00
$Error_b$	59†	127.9743	2.1691		

† One degree of freedom subtracted due to deletion of anomalous Spinks Block I Bt and C horizon data.

Differences between series in location of adsorption within the soil profile may be important in determining sensitivity to acid deposition. The Grayling, Rubicon, Kalkaska, and Montcalm series have large portions of adsorptive capacity concentrated in the uppermost 50 cm of their B horizons (Figure 5.7). Sulfate and associated

cations retained in this layer could be readily incorporated in nutrient cycling processes. Any sulfate and cations leached below this zone, especially in Grayling, Rubicon, and Kalkaska soils, would be subject to rapid loss from the soil because of the coarse texture and lower adsorption capacity in the 50-150 cm depths in these soils.

In contrast, Spinks and Oshtemo soils have adsorptive capacity distributed throughout the soil profile. Sulfate containing solutions would have a greater volume of soil with which to equilibrate, thus increasing likelihood of adsorption and retention of sulfate and associated cations. The calcareous C horizons (Table 5.1, Appendix B) in Montcalm, Spinks, and Oshtemo may be important in sulfate retention through co-precipitation of sulfate with $CaCO_3$, as well as providing large reserves of base cations well within the rooting zone of forest vegetation. The presence of Bt horizons in Montcalm, Spinks, and Oshtemo soils may be important in impeding rapid downward movement of percolating water, increasing soil:solution contact time and increasing opportunity for sulfate adsorption. The flow path of percolating waters through these soils is important in predicting the ultimate fate of sulfate in leaching solutions, as suggested by Johnson and Henderson (1979).

EXTRACTABLE SULFATE - INTER-SERIES COMPARISONS

An analysis of variance incorporating depth as a split plot factor was also utilized to compare levels of

extractable sulfate between series. Analysis of variance results are presented in Table 5.3. Extractable sulfate data were statistically analyzed as log [(g S m^{-2})+1].

Table 5.3

Analysis of Variance Results - Extractable Sulfate

Source	DF	SS	MS	F	P
Block	5	1.1858	0.2372	1.88	0.13
Series	5	2.0987	0.4197	3.33	0.02
$Error_a$	25	3.1482	0.1259		
Depth	2	1.5378	0.7689	41.15	0.00
Series x Depth	10	1.4069	0.1407	7.53	0.00
$Error_b$	60	1.1209	0.0187		

The significant Series x Depth interaction is shown in Figure 5.8. In the upper 50 cm of sulfate adsorbing horizons, higher contents of extractable SO_4-S in Rubicon as compared to Kalkaska, Montcalm, and Oshtemo suggest differences between series in ability to retain SO_4-S under field conditions. Differences between Rubicon and Oshtemo are similar to differences between these series in sulfate adsorption (Figure 5.7). Rubicon, Kalkaska, and Montcalm soils occur in the same geographic area of Michigan and would have received similar amounts of atmospheric SO_4-S deposition over time. Higher extractable sulfate in Rubicon soils may be related to higher S adsorption due to lower pH, lower organic matter, and lower base saturation in Rubicon

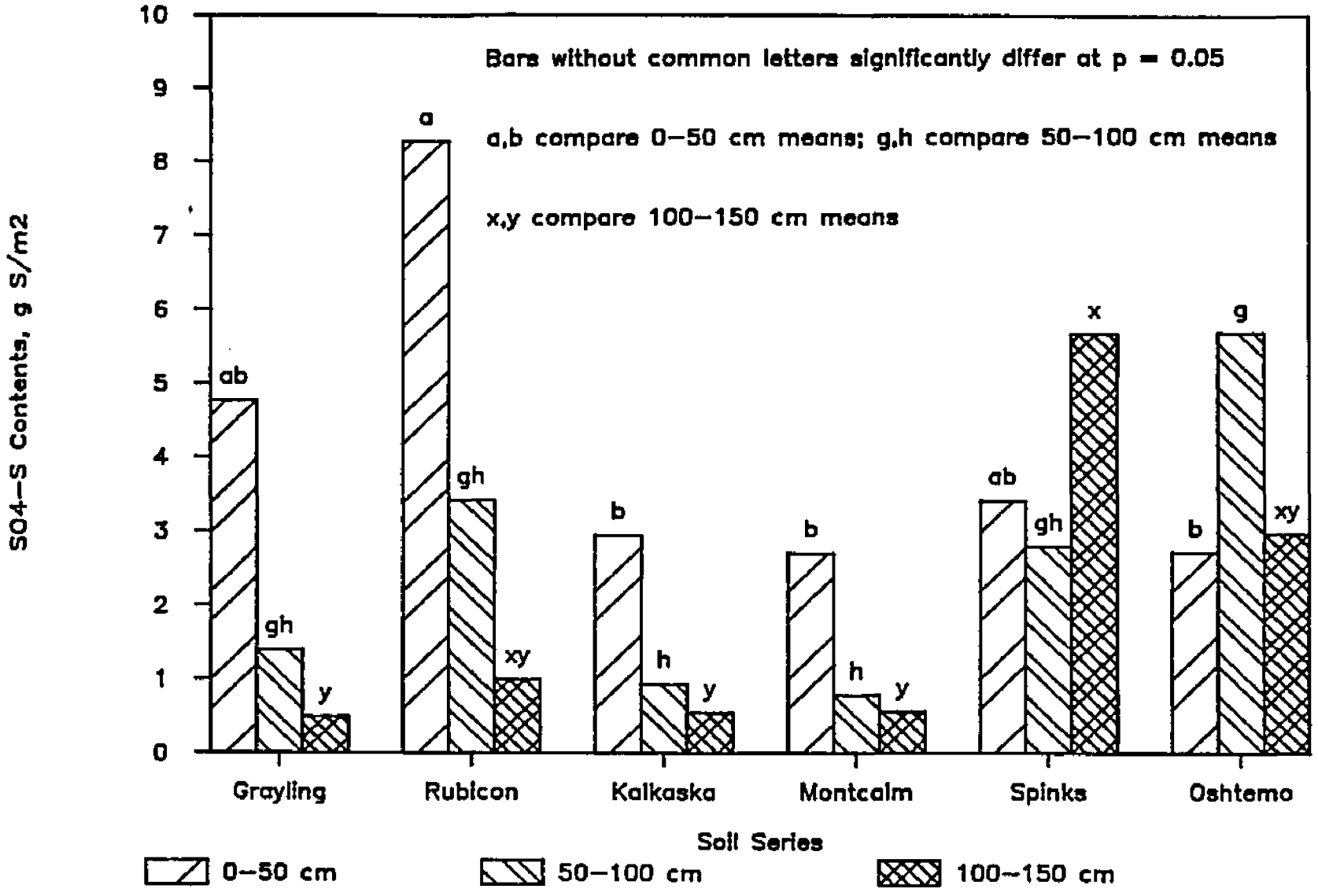

Figure 5.8

Extractable S - Series x Depth Interaction

than in Kalkaska and Montcalm soils, even though Al and Fe concentrations were similar (Table 5.1). Alternatively, lower sulfate contents in the Kalkaska and Montcalm series may indicate higher rates of microbial incorporation of SO_4-S into organic forms, again related to pH and organic matter differences (David et al., 1982; Strickland et al., 1986). The high extractable SO_4-S content of the Oshtemo series at the 50-100 cm depth and the Spinks series in the 100-150 cm depth (Figure 5.8) reflect the adsorption ability of the Bt horizons. Patterns in extractable sulfate contents with respect to depth support the contention that the major site of sulfate adsorption in frigid zone series is in the upper 50 cm of the B horizons, with limited amounts of sulfate retained below this point. In mesic zone series, sulfate is retained throughout the profile, significant amounts being adsorbed in Bt horizons.

EXTRACTABLE SULFATE CONTENTS - SOIL PEDONS

Extractable SO_4-S contents, calculated to a depth of 150 cm, ranged from 1.4 to 30.3 g S m^{-2} for individual pedons (Figure 5.9). When compared on a series basis (Appendix D, Table D.6; Table 5.4), extractable SO_4-S was higher in the Rubicon series than in the Kalkaska or Montcalm series. Differences among Rubicon, Kalkaska, and Montcalm are apparently related to series differences in sulfate retention. High, but variable SO_4-S levels in Spinks and Oshtemo soils may result from series differences

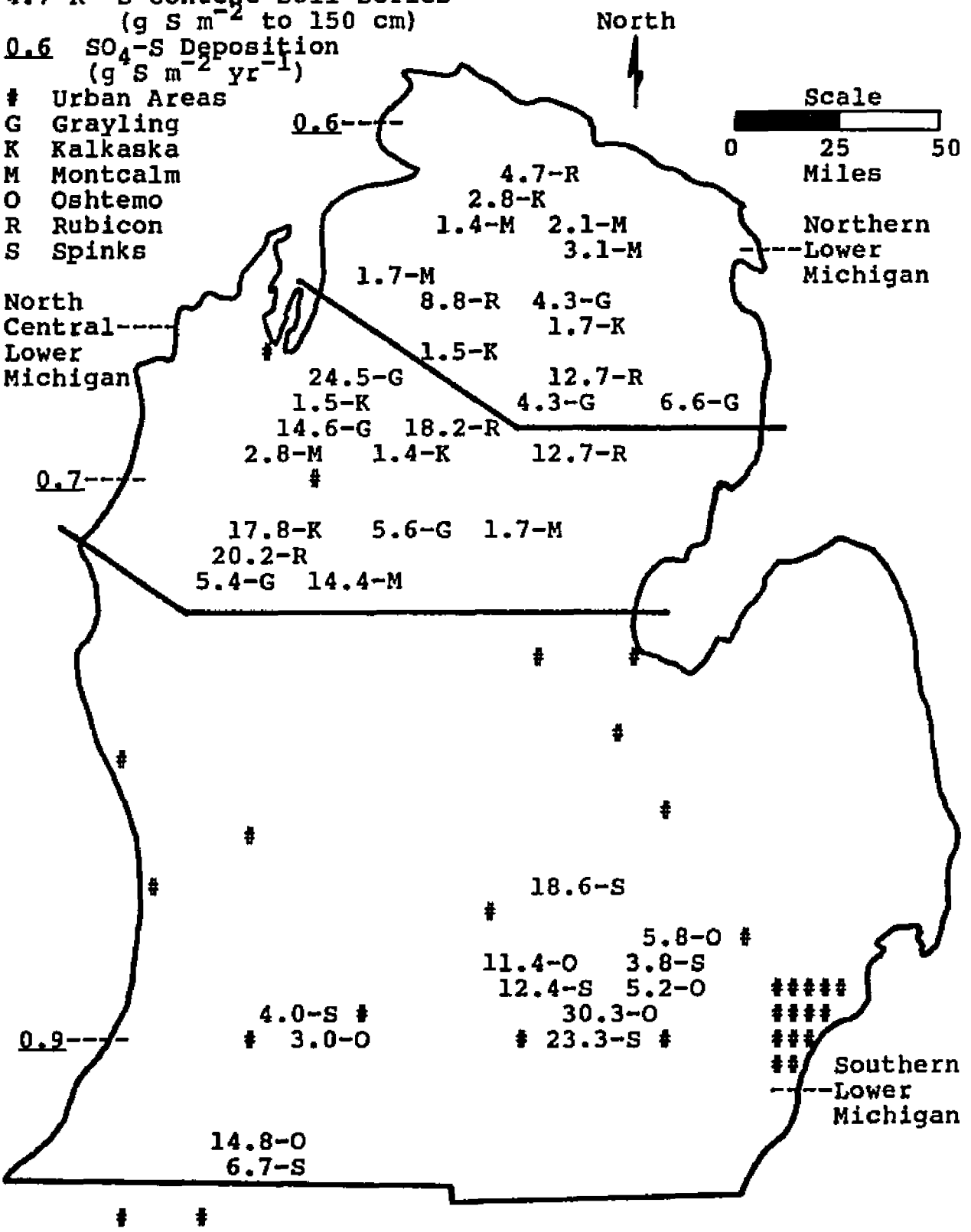

Figure 5.9

Sulfate-Sulfur Contents of Pedons to a Depth of 150 Centimeters

in adsorption in combination with higher variability in sulfate deposition, as a greater number of urban pollution sources are present in southern lower Michigan (Figure 5.9).

Table 5.4

Extractable Sulfate Contents to 150 cm by Soil Series

	Extractable SO_4-S†	
	Mean	Standard Deviation
Soil Series *	g S m^{-2}	
Grayling	6.8 ab	3.9
Kalkaska	4.5 b	6.5
Montcalm	4.2 b	5.0
Oshtemo	11.8 ab	10.1
Rubicon	12.9 a	5.8
Spinks	11.5 ab	8.1

* Means not followed by the same letter are significantly different at P = 0.05.

† Data statistically analyzed as log (g S m^{-2})

When pedons were placed into regional soil groups (Figure 5.9, Table 5.5), average extractable SO_4-S contents in southern lower Michigan forest soils were significantly higher than in northern lower Michigan forest soils, with north-central lower Michigan forest soils having intermediate SO_4-S contents (Appendix D, Table D.7). These results are consistent with the gradient of annual sulfate deposition from 0.9 g S m^{-2} in southern lower Michigan to

0.6 g S m^{-2} in northern lower Michigan (Figure 5.9; NADP, 1985b). Regional comparisons are tentative and made with caution since regional differences in soil SO_4-S content are confounded with block and series effects.

Table 5.5

Extractable Sulfate Contents to 150 cm by Geographic Region

Geographic Region *	Extractable SO_4-S† Mean (g S m^{-2})	Extractable SO_4-S† Standard Deviation (g S m^{-2})
Northern Lower Michigan‡	4.5 x	3.4
North-Central Lower Michigan‡	9.7 xy	7.3
Southern Lower Michigan	11.6 y	8.7

* Means not followed by the same letter are significantly different at P = 0.05.
† Data statistically analyzed as log (g S m^{-2})
‡ Data for Block 7 pedons not included in means

DISCUSSION

Mean values for sulfate adsorption, calculated on a series basis for the upper 150 cm of sulfate adsorbing horizons, ranged from 9.6 to 12.8 g S m^{-2}. Given an average annual wet sulfate deposition of 0.8 g S m^{-2} in the lower peninsula of Michigan (NADP, 1985a; 1985b; 1986), and assuming calculated adsorption values represent an adsorption capacity at present levels of deposition, calculations suggest Michigan forest soils could retain

sulfate and prevent acid deposition impacts related to sulfate leaching for a period of 12 to 16 years. Based on the range of calculated adsorption capacities for individual pedons (0.5 to 21.1 g S m^{-2} to 150 cm), individual soil bodies would have an ability to adsorb sulfate for periods from less than one to greater than 26 years at present rates of deposition.

This type of calculation is somewhat facile in light of the uncertainties involved in applying laboratory results to field situations, and does not account for microbial or plant uptake and cycling of SO_4-S. Previous investigators (Johnson and Henderson, 1979; Johnson et al., 1979a; Johnson, 1980; Johnson, D.W., et al., 1981) found that laboratory sulfate adsorption studies gave minimal indices of adsorptive capacity. Sulfate adsorption under field conditions was consistently greater than predicted from laboratory results. This suggests that estimates based on laboratory results should be conservative as to the adsorptive capacity of Michigan forest soils.

Relative reversibility of adsorption was not investigated, but even temporary adsorption of sulfate in the soil profile would permit re-uptake of associated nutrient cations by forest vegetation, enhance opportunities for microbial incorporation of SO_4-S into organic S forms, and encourage more permanent retention of sulfate over time through slow changes in sulfate-sesquioxide bonds or by initiating precipitation of Fe or Al hydroxy sulfate

minerals. These processes, alone or in combination, would serve to buffer or reduce rapid cation leaching losses resulting from excess H^+ and SO_4^{2-} in precipitation.

A "worst case scenario" for Michigan forest soils would be that sulfate is only temporarily retained, and readily displaced from the soil, resulting in equivalent leaching losses of basic cations. This situation would be present if Michigan soils were already in equilibrium with present levels of sulfate deposition so that sulfate inputs and outputs balanced. Under a "best case scenario," all sulfate deposited would be irreversibly adsorbed until all adsorption sites were filled, at which point leaching of sulfate and elevated loss of bases would commence.

It is unlikely, however, that all sulfate deposited would be retained by the soil. Indeed, relatively high mean sulfate concentrations in soil solution (10.8 to 17.3 mg S L^{-1}) and groundwater (11.6 to 17.6 mg S L^{-1}) in a variety of northern lower Michigan forest soils indicate this is not the case (Urie et al., 1986). This suggests that the relatively limited sulfate adsorption abilities of Michigan forest soils are capable of buffering, but not preventing, adverse cation leaching effects resulting from impingement of acid deposition.

The lack of significant differences between soil series in overall sulfate adsorptive ability and high variability within series suggest that a classification based on soil series may not be the best indicator of sulfate adsorbing

capacity, at least among soils considered sensitive to acid deposition based on low cation exchange capacity. More pronounced differences might be evident from adsorption determinations performed at higher sulfate concentrations, but present results suggest that variability would probably be as high within series as between series. The lack of significant differences between series also masks the fact that certain soil pedons were substantially lower than others in sulfate adsorbing ability, a factor of 40 separating the pedons with lowest (0.5 g S m^{-2}) and highest (21.1 g S m^{-2}) calculated adsorption capacities. When grouped solely by adsorption capacities, a total of 20 of the 38 pedons sampled adsorbed less than 10.0 g S m^{-2}, 12 adsorbed 11.0 to 15.1 g S m^{-2}, and 6 had adsorbing capacities between 15.9 and 21.1 g S m^{-2}. On this relative scale, the majority of the Michigan forest soils sampled would be classified as low to moderate sulfate adsorbers.

Actual differences between series may exist under field conditions that were not evident from laboratory results. These would include differences in microbial incorporation of sulfate into organic S forms, sulfate uptake and immobilization by forest vegetation, wetting-drying cycles dependent on soil moisture regimes, and influence of subsurface textures and horizons on flow path and retention time of percolating solutions. Qualitative differences between series important to sensitivity to acid deposition, such as those related to effects of water movement on

sulfate retention, would best be determined by field studies examining in situ sulfate fluxes within the soil profile.

Meaningful groupings of soils as to sulfate adsorptive abilities may be possible at higher soil taxonomic categories such as the family, subgroup, great group, or suborder levels. Soil differences might be more pronounced when comparing a wider variety of soils beyond those low in cation exchange capacity. Alternatively, an ecosystem approach incorporating vegetation, landform, soil, and regional differences in sulfate deposition to classify ecosystem sensitivity to acid deposition may be required.

SUMMARY AND CONCLUSIONS

All soil series studied had several horizons capable of adsorbing sulfate under laboratory conditions. Bw, Bs, and Bh horizons in frigid zone soils and E and Bt horizons in mesic zone soils displayed the highest sulfate adsorption. Total quantities of sulfate adsorbed and the small reductions in solution sulfate concentrations during adsorption equilibrations suggest that these soils are relatively weak sulfate adsorbers, similar to forest soils in the northeastern United States.

No significant differences were found between series in total amounts of sulfate adsorbed under laboratory conditions when compared on the basis of adsorbed sulfate contents calculated to a depth of 150 cm in sulfate adsorbing horizons. This suggests that a soil series level

classification may not be the best indicator of soil sensitivity to acid deposition in terms of overall sulfate adsorption ability. Significant differences between series in sulfate adsorption ability were present when comparing the upper 50 cm or the 100-150 cm depths in sulfate adsorbing horizons. Series differences in location of adsorption within the soil profile and flow path of percolating solutions may be more important in determining relative sensitivity to acid deposition than absolute differences in total amounts of sulfate adsorbed.

The consistent ability of all six series to adsorb sulfate from low concentration (10 mg S L^{-1}) sulfate solutions and positive correlations between adsorption and initial levels of extractable sulfate suggest that these series and similar Michigan forest soils are capable of retaining additional quantities of atmospherically deposited sulfate. Estimates based on calculated adsorptive capacites suggest that elevated leaching losses of basic cations resulting from acid deposition will not be prevented, but will be buffered, by sulfate adsorption in Michigan forest soils for time periods ranging from a few years to a few decades.

Chapter VI

RELATION OF SULFATE ADSORPTION TO SOIL PROPERTIES

This chapter discusses the relationships between sulfate adsorption and soil properties in Michigan forest soils. Simple correlations between soil properties and sulfate adsorption are presented and examined.

CORRELATIONS - ALL SERIES

Simple correlations between sulfate adsorption (mg S kg^{-1}) and other soil properties are presented in Table 6.1. Data from Bt and C horizons of the Block I Spinks pedon have been excluded due to their high release of SO_4-S during adsorption equilibrations. Sample correlation coefficients (r) are quite variable for small samples, particularly when the population correlation coefficient (rho) is at or near zero. For samples with n > 50, confidence belts for sample correlations are fairly narrow at values of rho > 0.50. In large samples, small values of r may be statistically, but not practically, significant (Steel and Torrie, 1980). Correlations discussed in this chapter are based on n > 50, exact sample size depending on grouping of data (Table 6.1). The size of the correlation matrix (21 soil properties x 4 soil horizon combinations) increases the likelihood that significant correlations will occur by chance. For this reason, discussion is limited to correlations having

Table 6.1

Correlations† Between Sulfate Adsorption and Soil Properties

	--- Correlation with S adsorbed (mg S kg^{-1}) in ---							
	All Series All Horizons		All Series Subsurface Horizons[1]		Mesic Zone Subsurface Horizons[2]		Frigid Zone Subsurface Horizons[3]	
Property[4]	r	P	r	P	r	P	r	P
DC-Fe	0.28	0.000	0.31	0.000	0.50	0.000	0.59	0.000
DC-Al	0.61	0.000	0.82	0.000	0.69	0.000	0.89	0.000
AO-Fe	0.37	0.000	0.67	0.000	0.59	0.000	0.78	0.000
AO-Al	0.63	0.000	0.79	0.000	0.69	0.000	0.90	0.000
NP-Fe	0.24	0.000	0.56	0.000	0.24	0.063	0.65	0.000
NP-Al	0.53	0.000	0.69	0.000	0.29	0.021	0.82	0.000
Exch-Al	0.19	0.003	0.66	0.000	0.58	0.000	0.79	0.000
Cr-Fe	0.21	0.002	0.14	0.060	0.45	0.000	0.21	0.021
pH-H_2O	-0.02	0.747	-0.56	0.000	-0.62	0.000	-0.52	0.000
pH-$CaCl_2$	-0.05	0.486	-0.53	0.000	-0.60	0.000	-0.50	0.000
Org-C	-0.58	0.000	0.60	0.000	0.21	0.094	0.70	0.000
Ext-S	0.36	0.000	0.59	0.000	0.68	0.000	0.57	0.000
Ext-P	0.08	0.233	0.17	0.024	0.01	0.911	0.39	0.000
Clay	N.D.‡	---	N.D.	---	0.65	0.000	N.D.	---
Exch-Ca	-0.23	0.000	-0.30	0.000	-0.32	0.010	-0.27	0.003
Exch-Mg	-0.19	0.003	-0.11	0.130	0.22	0.083	-0.20	0.033
Exch-K	-0.45	0.000	0.18	0.013	0.63	0.000	0.03	0.786
Exch-Na	-0.14	0.041	-0.04	0.551	0.25	0.051	-0.12	0.186
Σ Bases	-0.24	0.000	-0.29	0.000	-0.29	0.022	-0.27	0.003
Eff-CEC	-0.23	0.001	-0.24	0.001	-0.23	0.070	-0.23	0.013
Base Sat	-0.43	0.000	-0.51	0.000	-0.43	0.000	-0.54	0.000
n	229		180		62		118	

† Spinks Block I Bt and C horizon data excluded due to high S release during adsorption equilibrations

1 Excludes frigid zone A, A/E, and E horizons and mesic zone A and Ap horizons.

2 Spinks and Oshtemo Series; excludes A and Ap horizons.

3 Grayling, Rubicon, Kalkaska, and Montcalm Series; excludes A, A/E, and E horizons; includes Grayling and Montcalm "Block 7" pedons.

4 Units: pH in $-Log(H^+)$; Org-C, Clay, Base Sat in %; Σ Bases, CEC in cmol (+) kg^{-1}; all others in mg kg^{-1}

‡ N.D. - % clay not determined for surface horizons or frigid zone subsurface horizons.

theoretical relationships with sulfate adsorption or to those previously reported in the literature.

For all series and soil horizons combined (Table 6.1), the soil properties with the strongest positive correlations with sulfate adsorption were dithionite-citrate extractable Al (DC-Al, r = 0.61), ammonium oxalate extractable Al (AO-Al, r = 0.63), and Na-pyrophosphate extractable Al (NP-Al, r = 0.53). Figure 6.1 shows that a high degree of scatter exists at lower AO-Al concentrations, partly due to the inclusion of surface horizons low in AO-Al (Table 5.1, Appendix B) that exhibited sulfate release during equilibration. Organic carbon was negatively correlated (r = -0.58) with sulfate adsorption (Figure 6.2). The negative correlation exists largely due to separate clustering of high organic carbon, sulfate-releasing surface horizons, and sulfate-adsorbing subsurface horizons lower in organic carbon (Table 5.1, Appendix B). This correlation supports the contention that organic matter interferes with sulfate adsorption (Johnson and Todd, 1983; Evans, 1986), but only insofar as it applies to differences in sulfate retention between surface horizons and subsurface horizons.

Correlations based on combined data for all soil horizons are misleading because surface horizons and subsurface horizons differ in mode of sulfate retention. Results of the current study (Chapter V) indicated that surface horizons of frigid zone (A, A/E, E) and mesic zone (A) soils were not strongly active in physico-chemical

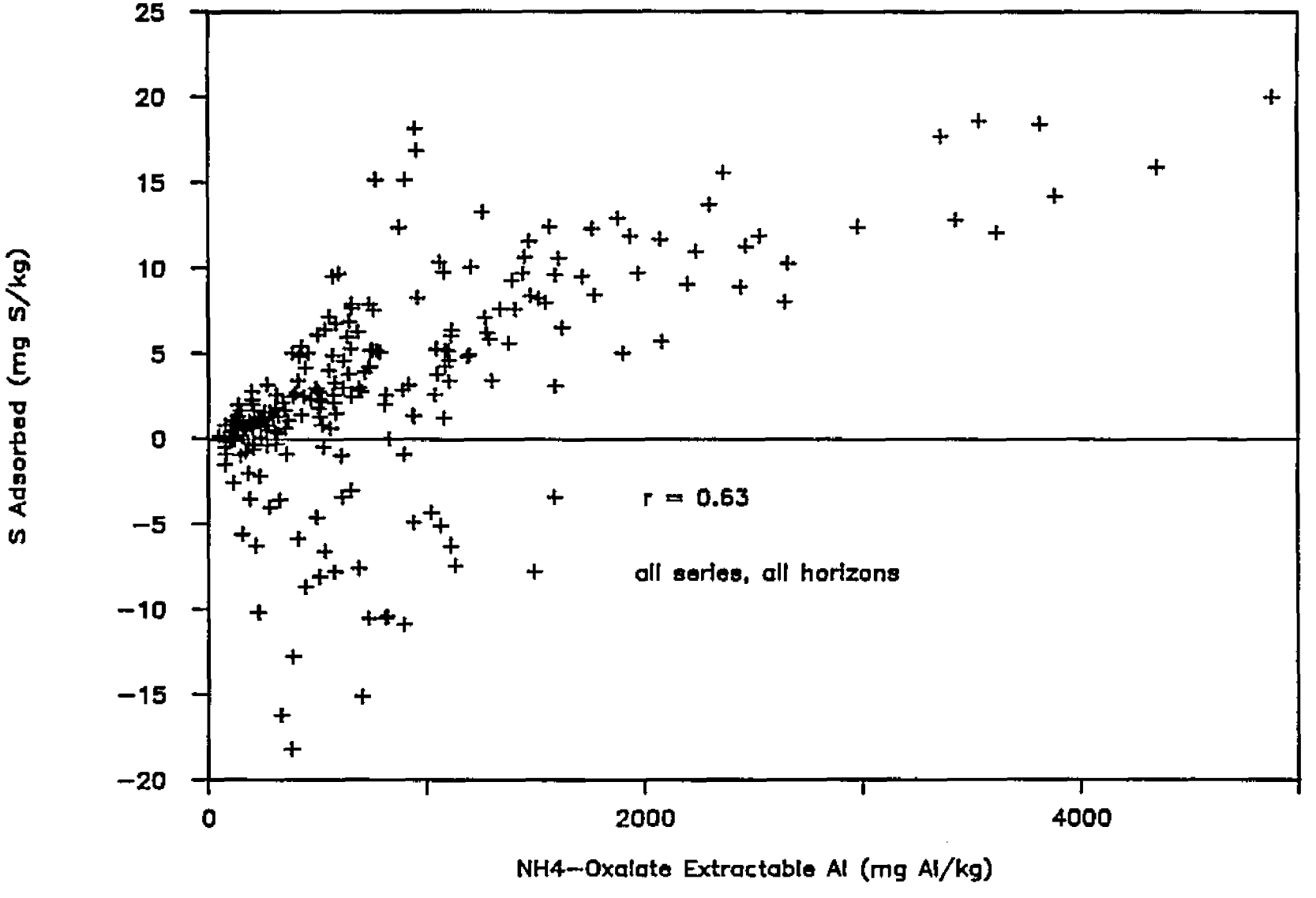

Figure 6.1

Correlation of S Adsorbed with Ammonium Oxalate Extractable Al - All Series, All Horizons

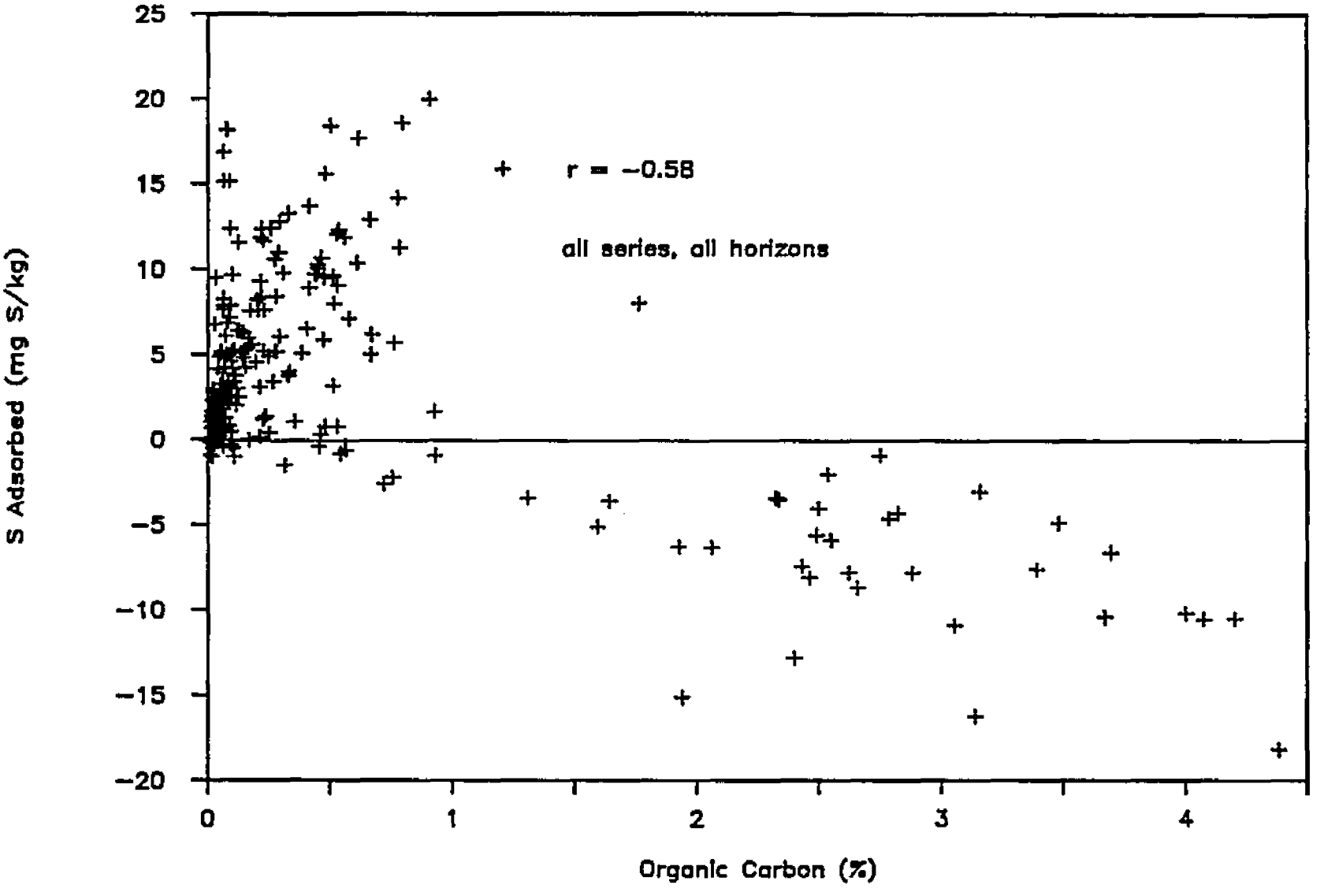

Figure 6.2

Correlation of S Adsorbed with % Organic Carbon - All Series, All Horizons

adsorption processes. Sulfate retention in surface horizons is largely a microbially mediated process (Fitzgerald and Strickland, 1982; David et al., 1983), with sulfate release increased by mineralization of organic S during air-drying (Freney, 1958; David et al., 1982). Surface horizons are important because the amount of sulfate reaching underlying B horizons depends on S cycling patterns and transfer within these soil layers. While important to overall S cycling, these processes are beyond the scope of the present study. Subsequent discussion will be restricted to subsurface horizons where adsorption related to soil physical and chemical properties is a major factor in sulfate retention.

Correlations between sulfate adsorption and soil properties in subsurface horizons of all series combined are presented in Table 6.1. Strongest correlations were with the extractable aluminum fractions, DC-Al ($r = 0.82$), AO-Al ($r = 0.79$), NP-Al ($r = 0.69$), and exchangeable Al ($r = 0.66$); r values increased after exclusion of surface horizon data. Figure 6.3 shows the correlation between sulfate adsorption and AO-Al. The improvement in the relation due to exclusion of surface horizon data is apparent when compared with Figure 6.1. Exclusion of surface horizon data also improved correlations (Table 6.1) between sulfate adsorption and ammonium oxalate extractable Fe (AO-Fe, from $r = 0.37$ to 0.67) and Na-pyrophosphate extractable Fe (NP-Fe, from $r = 0.24$ to 0.56).

Negative correlations existed between sulfate

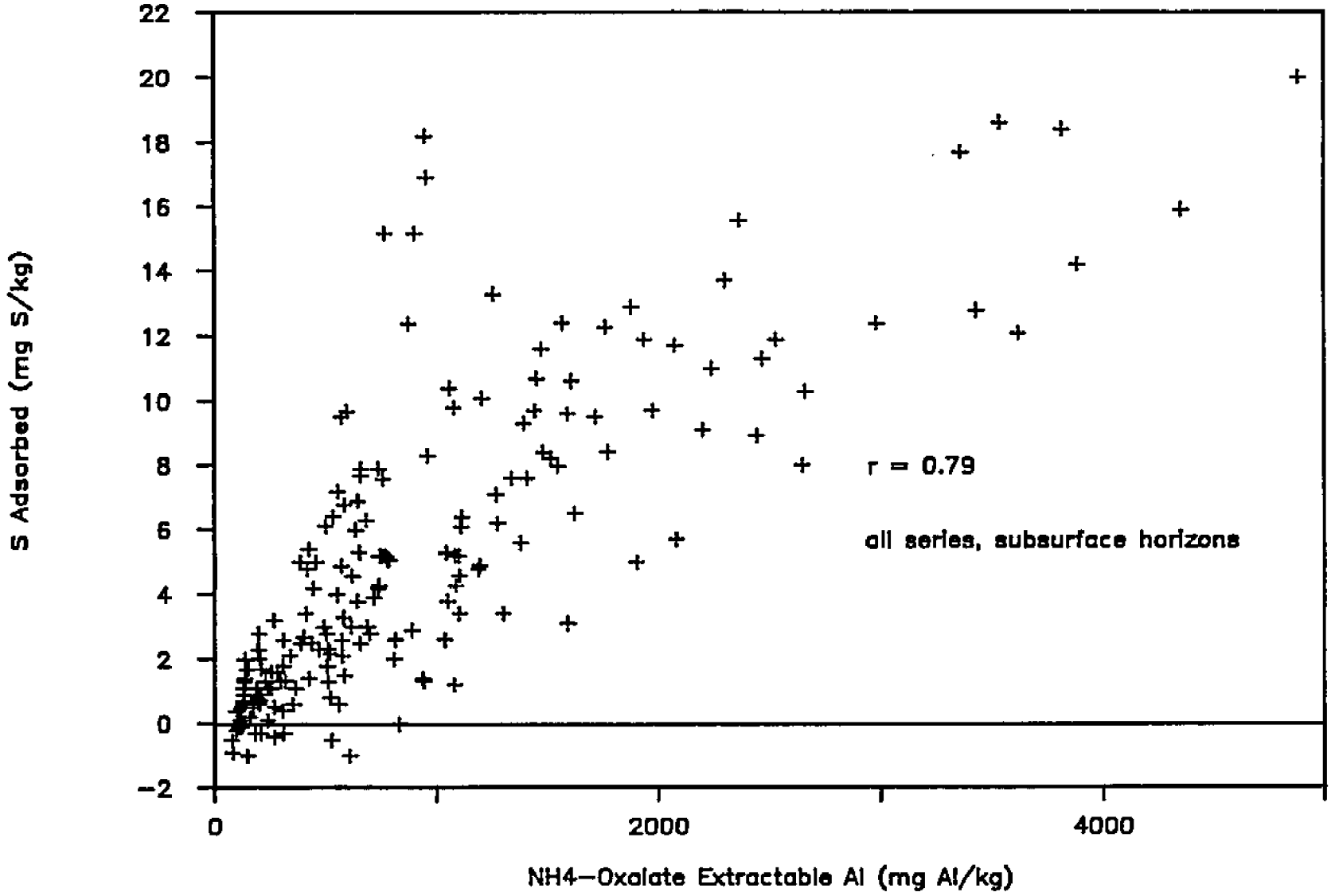

Figure 6.3

Correlation of S Adsorbed with Ammonium Oxalate Extractable Al - All Series, Subsurface Horizons

adsorption and pH-H_2O (r = -0.56), pH-$CaCl_2$ (r = -0.53), and base saturation (r = -0.51). Sulfate adsorption in subsoils of a variety of Australian soils was also negatively correlated (r = -0.82) with pH (Williams and Steinbergs, 1962). Figure 6.4 shows that the relationship of pH-H_2O with sulfate adsorption was curvilinear. A negative pH effect is expected, as reported by Kamprath et al. (1956), Chao et al. (1963), and Parfitt (1982). The curvilinear trend is similar to curves reported by Chao et al. (1964) and closely matches the pH - sulfate adsorption relationship depicted by Barrow et al. (1969). The curvilinearity may be related to the effect of pH being greater in horizons containing higher amounts of sesquioxides, as reported by Chao et al. (1963). The wide range in sulfate adsorption evident between pH 4.5 and 6.0 may reflect the wide range in sesquioxide concentrations in horizons with these pH values. The negative correlation with base saturation is related to the pH effect (pH-H_2O:base saturation r = 0.70), as well as to findings that Al^{3+} saturation of soil increased sulfate retention, while saturation of soil by Ca^{2+}, K^+, or Na^+ decreased sulfate retention, the cation effect being in addition to the pH effect (Chao et al., 1963).

CORRELATIONS - MESIC AND FRIGID ZONE SOILS

Results of inter-series comparisons of sulfate adsorption (Chapter V) indicated that different patterns of adsorption occurred in mesic zone series (Spinks, Oshtemo)

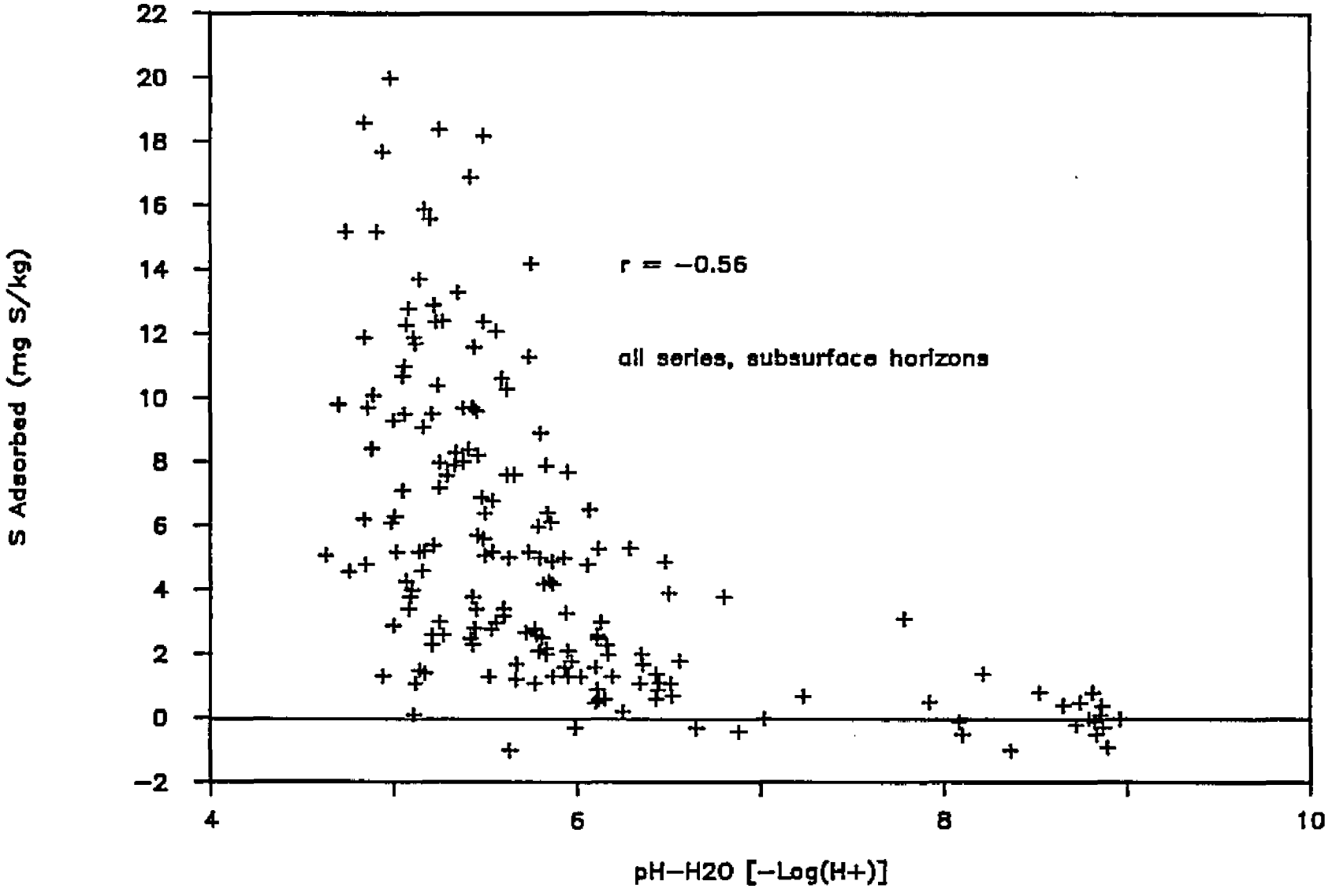

Figure 6.4

Relation of S Adsorbed to pH-H_2O

than in frigid zone series (Grayling, Rubicon, Kalkaska, Montcalm). Separate correlations for subsurface horizons of these two groups are presented in Table 6.1. In mesic zone subsurface horizons (E, B, E', C), sulfate adsorption was positively correlated with dithionite-citrate extractable Fe (DC-Fe, r = 0.50), DC-Al (r = 0.69), AO-Fe (r = 0.59), AO-Al (r = 0.69), exchangeable Al (r = 0.58), crystalline Fe (Cr-Fe, DC-Fe - AO-Fe, r = 0.45), and % clay (r = 0.65). Figure 6.5 shows that the relationship of sulfate adsorption with AO-Al in mesic zone soils exhibits high scatter at higher AO-Al concentrations, suggesting that other factors modify the effect of increasing AO-Al concentration on adsorption. Sulfate adsorption in mesic zone subsurface horizons was negatively correlated with pH-H_2O (r = -0.62), pH-$CaCl_2$ (r = -0.60), and base saturation (r = -0.43).

In frigid zone subsurface horizons (B, E', C), sulfate adsorption was strongly correlated with DC-Al (r = 0.89), AO-Al (r = 0.90), NP-Al (r = 0.82), and exchangeable Al (r = 0.79), all correlations being higher than in mesic zone subsurface horizons. The relationship between sulfate adsorption and AO-Al is depicted in Figure 6.6. Correlations with all extractable Fe fractions, except Cr-Fe (r = 0.21), were higher than in mesic zone subsurface horizons (DC-Fe, r = 0.59; AO-Fe, r = 0.78; NP-Fe, r = 0.65). Sulfate adsorption was positively correlated ($P < 0.01$, n = 118) with organic carbon (r = 0.70) in frigid zone subsurface horizons, possibly an artifact due to

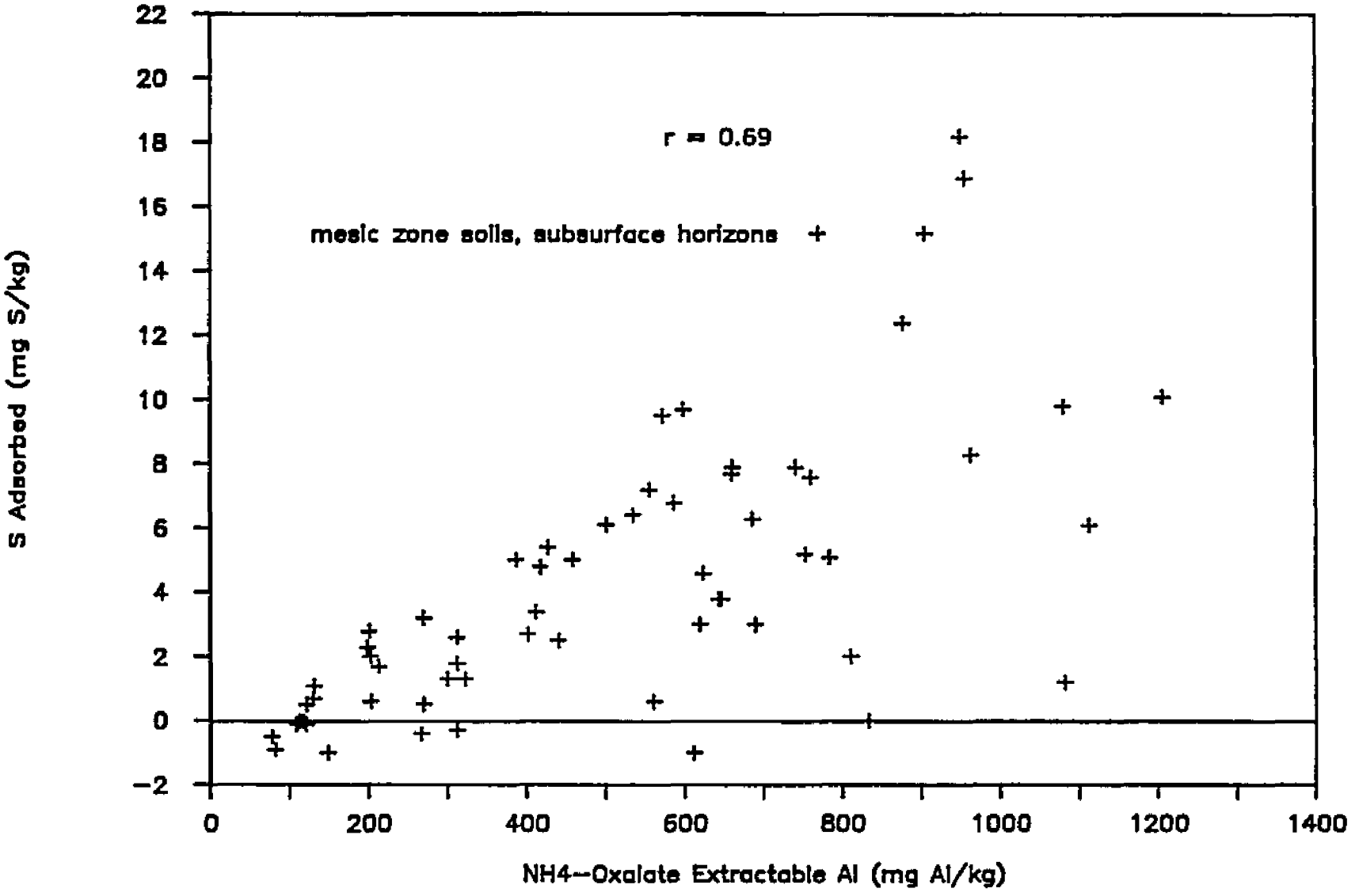

Figure 6.5

Correlation of S Adsorbed with Ammonium Oxalate Extractable Al - Mesic Zone Soils, Subsurface Horizons

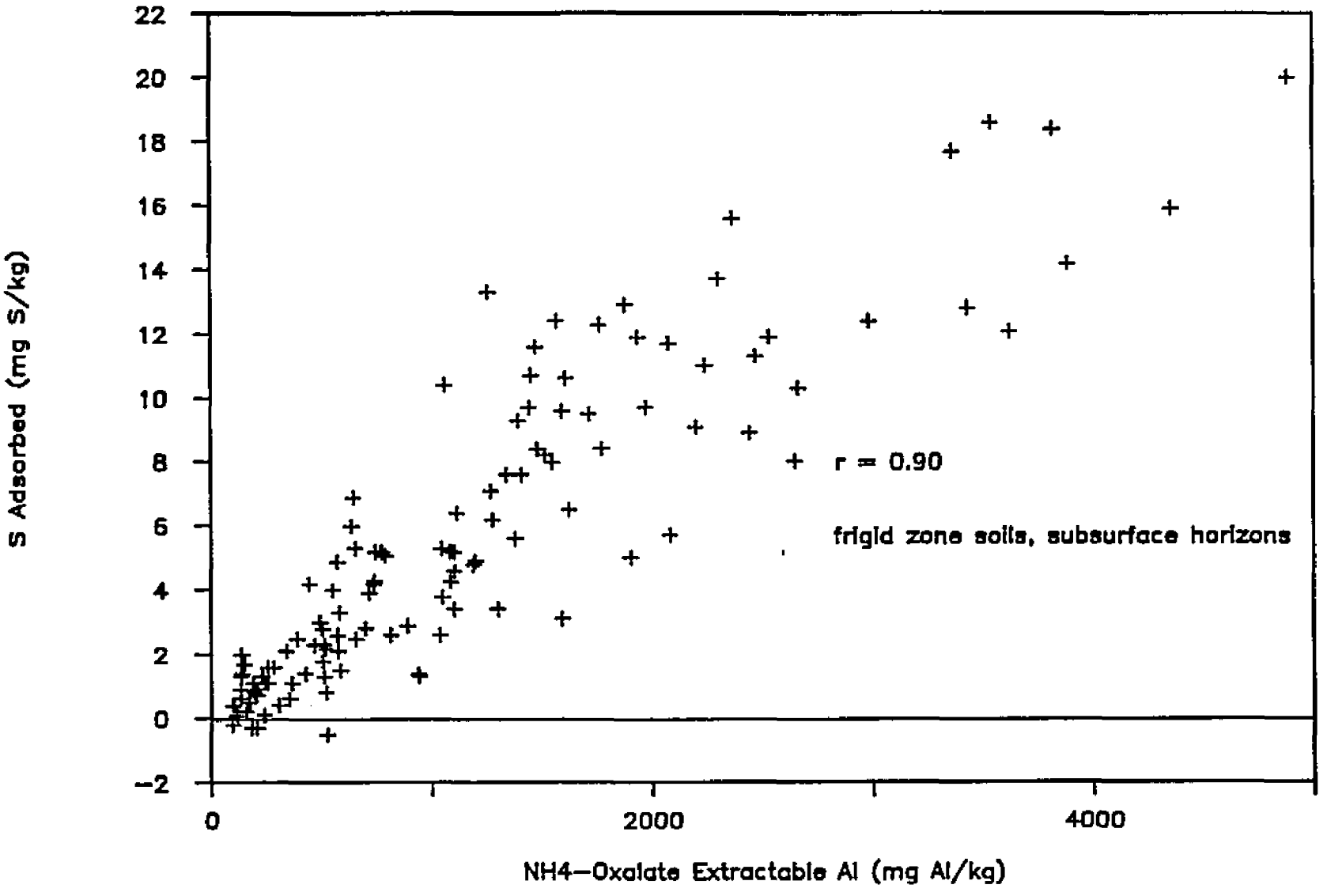

Figure 6.6

Correlation of S Adsorbed with Ammonium Oxalate Extractable Al - Frigid Zone Soils, Subsurface Horizons

correlations between organic carbon and DC-Al (r = 0.89), AO-Al (r = 0.78), NP-Al (r = 0.93), and exchangeable Al (r = 0.83). Alternatively, positive correlation with organic carbon could be related to microbial incorporation of sulfate into organic S forms (David et al., 1982; Strickland et al., 1986). Negative correlations with sulfate adsorption existed for base saturation (r = -0.54), pH-H_2O (r = -0.52), and pH-$CaCl_2$ (r = -0.50), similar to those found for mesic zone subsurface horizons.

Comparison of Figures 6.5 and 6.6 shows that in mesic zone soils the relationship between sulfate adsorption and AO-Al differed from that in frigid zone soils, the slope being steeper and scatter greater in mesic zone soils. AO-Al concentrations in subsurface horizons of mesic zone soils were generally lower than those in frigid zone soils (Table 5.1, Appendix B). Stronger negative correlations with pH, stronger positive correlation with Cr-Fe, positive correlation with % clay, and weaker correlations with all other extractable Al and Fe fractions in mesic zone soils suggest that sulfate adsorption in mesic soils is affected by a complex of soil properties. When segregated from mesic zone data, improved correlations between sulfate adsorption and soil properties in frigid zone soils suggest that grouping dissimilar soils, even when sampled from a small geographic area, may obscure relationships evident when soils are placed in groups based on morphologic, taxonomic, and ecologic similarity.

Lower correlations found for mesic zone soils may be the result of influences related to disturbance history. Forest stands sampled in southern lower Michigan were older (mean age = 85 years) but with greater variability in age (standard deviation = ±33 years) than forest stands sampled in northern lower Michigan (62 ± 12 years), suggesting that disturbance patterns have been different in these two regions. Early settlement, resulting in land clearing, cultivation, and grazing, greatly influenced southern lower Michigan forests. In contrast, disturbance in northern lower Michigan forests largely involved logging and fire, followed by regrowth of vegetation with a minimum of further soil disturbance. Several pedons in southern lower Michigan had Ap horizons (Appendix B), indicative of cultivation, grazing, or similar soil disturbance prior to reforestation. In some cases, mesic zone soils may have been limed or otherwise amended prior to abandonment at various times in excess of 40 years ago. Based on extractable sulfate contents in pedons (Figure 5.9, Table 5.5), atmospheric sulfate deposition has been more variable in southern lower Michigan than in northern lower Michigan. These factors in combination may explain the lower correlations noted for mesic zone soils as past disturbance and variable sulfate deposition produced more diverse combinations of soil properties than in frigid zone soils.

Consistent correlation between sulfate adsorption and extractable Al and Fe fractions is in accord with the view

that sulfate is adsorbed through anion or ligand exchange reactions involving hydroxy Al and Fe oxides (Chao et al., 1965; Rajan, 1978), although precipitation of Al or Fe hydroxy sulfates might also be involved (Adams and Rawajfih, 1977; Adams and Hajek, 1978; Wolt and Adams, 1979; Wolt, 1981; Weaver et al., 1985). Higher correlations with Al than with Fe agreed with findings by Ensminger (1954), Chao et al. (1964), and Aylmore et al. (1967) that Al oxides were more effective in retaining sulfate than Fe oxides or minerals. Other authors (Barrow, 1967; Haque and Walmsley, 1973; Singh, 1980b; Fuller et al., 1985) have also found that correlations between sulfate adsorption and Fe fractions (r = 0.00 to 0.62) were non-significant or lower than correlations with various extractable Al fractions (r = 0.73 to 0.87). In contrast to observations by Johnson and Todd (1983, r = 0.69 to 0.73) and Fuller et al. (1985, r = 0.42 to 0.96), Cr-Fe was not strongly correlated (r = 0.21 to 0.45) with sulfate adsorption in subsurface horizons of the Michigan forest soils studied. High correlations with DC-Al and AO-Al suggest that the Al fractions removed by these extractants may be more active in sulfate adsorption than organically bound Al removed by Na-pyrophosphate. Similarly, higher correlations with AO-Fe than with Cr-Fe, DC-Fe, or NP-Fe suggest that inorganic amorphous Fe is most active in sulfate adsorption. While speculative, these relationships are similar to the results of Johnson et al. (1986), where highest sulfate adsorption was found in soils

highest in ammonium oxalate extractable Al and Fe.

Other studies (Haque and Walmsley, 1973; Singh, 1980b; Johnson and Todd, 1983; Fuller et al., 1985) indicated a lack of correlation between pH, organic carbon, or clay with sulfate adsorption, in contrast to the present study where significant correlations were found with all three properties. In previous studies, lack of correlation may be the result of small sample size (Haque and Walmsley, 1973; Singh, 1980b; Fuller et al., 1985), grouping of dissimilar soils (Haque and Walmsley, 1973; Johnson and Todd, 1983), inclusion of both surface and subsurface horizons (Singh, 1980b; Johnson and Todd, 1983), relating soil properties to insoluble adsorbed sulfate (Johnson and Todd, 1983; Fuller et al., 1985), or differences between properties of soils previously studied and properties of Michigan forest soils. In the present study, significant correlations involving pH and clay were in accord with generally accepted theory, and were based on relationships between soil properties in similar soils sampled with replication over a fairly small geographic region. Positive correlation between sulfate adsorption and organic carbon in frigid zone soils may be an artifact of high correlation between organic carbon and extractable Al and Fe fractions, or may be related to microbial transformations of sulfate to organic S forms.

Not considered in the present study was a measure of adsorptive capacity calculated as the sum of extractable sulfate and sulfate adsorbed under laboratory conditions.

Such a calculation assumes extractable sulfate represents adsorbed sulfate present in the soil, while sulfate extractions as performed would also remove any soluble sulfate present. Preliminary statistical analyses based on the sum of extractable and adsorbed sulfate indicated that comparisons between soil series (Chapter V) and relationships to soil properties (Chapter VI) were similar to those based solely on sulfate adsorbed under laboratory conditions.

SUMMARY AND CONCLUSIONS

Soil properties with the strongest positive correlations with sulfate adsorption for all series and horizons were dithionite-citrate extractable Al and ammonium oxalate extractable Al. Strength of correlations increased after exclusion of surface horizon data, because of differences in mode of sulfate retention between surface and subsurface horizons. Exchangeable Al, dithionite-citrate extractable Fe, and ammonium oxalate extractable Fe were also positively correlated with sulfate adsorption in subsurface horizons of mesic and frigid zone soils. Both pH-H_2O and pH-$CaCl_2$ were negatively related to sulfate adsorption in subsurface horizons of the series studied. Correlations between sulfate adsorption and soil properties were stronger in frigid zone soils than in mesic zone soils, possibly as a result of past disturbance producing higher variability in the soil properties of mesic zone series.

Chapter VII

PREDICTION OF SULFATE ADSORPTION IN FOREST SOILS

One of the problems associated with classifying sensitivity of Michigan forest soils to acid deposition is that measurements of sulfate adsorption ability have not been included in previous soil characterization studies. Fairly extensive soil characterization data exists that has been used to classify Michigan soils based on other soil chemical and physical properties (SCS-USDA, 1980; MTU-FFC, 1982-1984). The object of this chapter is to develop regression equations and linear discriminant functions for use in predicting sulfate adsorption using other commonly measured soil properties as predictor and discriminant variables. Selected regression equations and discriminant functions are presented and discussed.

REGRESSION ANALYSIS

Sulfate adsorption data and predictor variable data both required transformation to approximate normality, control variance, and maintain or improve linearity of relationships. Sulfate adsorption data included values below 1.0 as well as a few negative numbers. Transformation took the form $\ln[(\text{mg S kg}^{-1})+2]$, the constant being added to adjust values to a positive scale above 1.0 before taking logs (Mosteller and Tukey, 1977; Steel and Torrie, 1980).

Transformation of predictor variables other than pH measures took the form ln(X), although ln(X+1) was used when raw data included zero values or values below 1.0. Variables included in regression equations are described in Table 7.1.

Stepwise multiple regression techniques were used to screen predictor variables. Residuals were graphed in overall plots (frequency distributions), and against predicted Y values, predictor (X) variables, and various descriptive codes (e.g. series, soil horizon). Residual plots were examined for patterns indicating departure from linearity, non-homogeneity of variance, presence of influential observations, and need for extra predictor variables (Chatterjee and Price, 1977; Seber, 1977; Draper and Smith, 1980). Predictor variables that created problems of non-homogeneity of variance, non-normality, excessive multicollinearity, or involved relationships dependent on location of only a few data points were excluded from final regression equations. Total avoidance of multicollinearity was prevented because of the presence of inter-correlations among most soil properties. Higher order terms and interaction terms were included in test regressions, but in general they did not improve predictive ability and so they have been excluded for simplicity. Reported R^2 values are the unadjusted coefficients of multiple determination. Sequential R^2 values are the incremental values of R^2 obtained as independent variables were added to equations by stepwise regression procedures.

Table 7.1

Variables Included in Final Regression Equations

Dependent Variable† (All Regressions)	Soil Property	Base Units
Ln(S-Ads+2)	SO_4-S Adsorbed from 10 mg S L^{-1} solution	mg S kg^{-1}
Predictor Variables†	**Soil Property**	**Base Units**
Ln(AO-Al)	Ammonium Oxalate Extractable Al	mg Al kg^{-1}
Ln(AO-Fe)	Ammonium Oxalate Extractable Fe	mg Fe kg^{-1}
Ln(Cr-Fe)	Crystalline Fe (DC-Fe - AO-Fe)	mg Fe kg^{-1}
Ln(DC-Al)	Dithionite-Citrate Extractable Al	mg Al kg^{-1}
Ln(DC-Fe)	Dithionite-Citrate Extractable Fe	mg Fe kg^{-1}
Ln(Ex-Al+1)	Exchangeable Al	mg Al kg^{-1}
Ln(Ext-P)	Bray #1 Extractable P	mg P kg^{-1}
Ln(Ext-S)	Phosphate Extractable SO_4-S	mg S kg^{-1}
Ln(%Clay)	Clay Fraction, < 0.002 mm	%
Ln(Org-C)	Organic Carbon	mg C kg^{-1}
Ln(ΣBases+1)	Sum of Exchangeable Bases (Ca,Mg,K,Na)	cmol (+) kg^{-1}
pH-$CaCl_2$	pH measured in 0.01 M $CaCl_2$	-Log(H^+)
pH-H_2O	pH measured in H_2O	-Log(H^+)

† Ln denotes natural logarithm of base units
+1, +2 denote constants added to base units before transformation to log scale

A robust multiple regression program (Hintze, 1985) using Tukey's biweights (Mosteller and Tukey, 1977) was used to identify outliers in previously developed regression equations. Outliers assigned zero weights by robust regression were excluded from regression analyses when reasons for deviation could be identified. Table 7.2 describes outliers removed from various regression equations and summarizes reasons for departure from typical behavior. Examination of Table 7.2 reveals that outliers were typified by over-prediction of sulfate adsorption by regression equations. Outliers exhibited higher sulfate release or lower sulfate adsorption than similar samples from other pedons. Factors associated with non-typical behavior were high base saturation, high extractable S, high extractable P, or a combination of these factors. Specific outliers removed from each regression analysis are identified in the text by sample number. Soil characterization data for all samples can be found in Appendix B.

REGRESSION EQUATIONS

Surface horizons were found to release sulfate during adsorption equilibrations. Correlation analysis indicated that inclusion of these data obscured relationships between sulfate adsorption and most soil properties. The body of evidence indicates that surface horizons are relatively inactive in physico-chemical adsorption processes (Chapter VI). For these reasons, data from frigid zone A, A/E, and E

Table 7.2

Summary of Outliers Removed from Regression Equations

S.N.[1]	Series	S.H.[2]	Sign[3]	Probable Cause of Deviation[4]
3550	Montcalm	Bt	-	S release, high b.s.
4250	Oshtemo	BC	-	S release, high b.s.
4480	Oshtemo	C	-	S release, high extr. S & b.s.
4520	Oshtemo	E1	-	Low S ads., high extr. P
4530	Oshtemo	E2	-	S release, high extr. P & b.s.
4540	Oshtemo	Bt1	-	Low S ads., high extr. P & b.s.
4550	Oshtemo	Bt2	-	Low S ads., high extr. P & b.s.
4560	Oshtemo	BC	-	Low S ads., high extr. P & b.s.
6150	Spinks	Bt	-	High S release, extr. S & b.s.
6160	Spinks	C	-	High S release, extr. S & b.s.
6460	Spinks	C	-	S release, high b.s.

1 Sample Number
2 Soil Horizon
3 Sign of residual, - = over-prediction of S adsorption
4 S release = release of sulfate during adsorption equilibration, S ads. = sulfate adsorption, b.s. = base saturation, extr. S = phosphate extractable S, extr. P = Bray extractable P.

horizons and mesic zone A horizons were excluded from regression analyses. A variety of regression equations are presented to show the variety of variables and combinations of variables with predictive power. The number of equations presented also reflects the need for equations based on different predictor variables given present limitations in data availability (Chapter VIII). Models presented are empirical, but are based on theoretical relationships between sulfate adsorption and soil properties.

Table 7.3 presents results of regression analysis relating sulfate adsorption to soil properties in subsurface horizons of all series combined. The positive influence of AO-Al and DC-Fe on sulfate adsorption was expected, as was the negative effect of increasing pH. Outliers removed were 3550, 4250, 4480, 4520, 4530, 4540, 4550, 6150, and 6160. Size of standardized parameter estimates suggest that AO-Al (0.609) was most important in predicting sulfate adsorption in a variety of soil series, with its influence modified by DC-Fe (0.285) and pH (-0.304).

Results of correlation analyses indicated that combining data from a variety of soil series obscured relationships between sulfate adsorption and soil properties. For this reason, data were successively split into groups based on taxonomic, regional, and morphologic similarities and regression equations developed to predict sulfate adsorption within the separate groups. One reasonable split appeared to be into Alfisols (Montcalm,

Table 7.3

Regression for Subsurface Horizons - All Series

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	-1.7647				
Ln(AO-Al)	0.4244	0.0246	17.28	0.000	0.7465
pH-$CaCl_2$	-0.2081	0.0233	-8.94	0.000	0.7965
Ln(DC-Fe)	0.2434	0.0247	9.84	0.000	0.8706

R^2 = 0.87 S.E.† = 0.2434 EDF‡ = 169 F = 379.12 P = 0.000

† Standard Error of the Estimate (Ln units)
‡ Error Degrees of Freedom

Table 7.4

Regression for Alfisol Subsurface Horizons

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	-0.4387				
Ln(AO-Al)	0.3687	0.0599	6.15	0.000	0.5986
pH-$CaCl_2$	-0.1323	0.0424	-3.12	0.002	0.7386
Ln(Ex-Al+1)	0.2218	0.0363	6.12	0.000	0.7596
Ln(Org-C)	-0.2268	0.0446	-5.08	0.000	0.7847
Ln(AO-Fe)	0.3026	0.0507	5.96	0.000	0.8222
Ln(Ext-P)	-0.1907	0.0331	-5.77	0.000	0.8702

R^2 = 0.87 S.E.† = 0.2603 EDF‡ = 90 F = 100.53 P = 0.000

† Standard Error of the Estimate (Ln units)
‡ Error Degrees of Freedom

Spinks, Oshtemo) and the Entic-Spodic continuum of sandy, frigid zone soils comprising the Grayling, Rubicon, and Kalkaska series.

Results of regression analysis for the Alfisol group are presented in Table 7.4. Outliers removed were 4480, 6150, 6160, and 6460. It is apparent that a variety of factors are related to sulfate adsorption in these soils. Positive influences were related to AO-Al, exchangeable Al, and AO-Fe, evidence of the importance of anion or ligand exchange retention of sulfate on hydrous Al and Fe oxides. Soil pH ($CaCl_2$) exerted a negative influence. Of interest are the significant negative effects of both organic carbon and extractable P. Organic carbon has been cited as interfering with sulfate retention (Johnson and Todd, 1983; Evans, 1986), while phosphate strongly competes with sulfate for adsorption sites (Chao, 1964; Metson and Blakemore, 1978; Parfitt, 1982). The number of predictor variables included reflects the variability in soil properties inherent in combining data from a variety of soils. While this equation provides a good descriptive explanation for influences on sulfate adsorption in Alfisols, its predictive value is reduced by the number of predictor variables required as well as by correlation between predictor variables producing inflation of standard errors of parameter estimates.

Several regression equations were developed for soils in the Entic-Spodic group (Table 7.5). No outliers were

Table 7.5

Regressions for Entic-Spodic Subsurface Horizons

Entic-Spodic Regression A

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	-2.2723				
Ln(DC-Al)	0.6560	0.0287	22.85	0.000	0.8686
R^2 = 0.87	S.E.† = 0.2285	EDF‡ = 79	F = 522.35	P = 0.000	

Entic-Spodic Regression B

Predictor+ Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	-4.1040				
Ln(AO-Al)	0.5151	0.0332	15.52	0.000	0.8293
Ln(Cr-Fe)	0.3721	0.0584	6.37	0.000	0.8878
R^2 = 0.89	S.E.† = 0.2125	EDF‡ = 78	F = 308.46	P = 0.000	

Entic-Spodic Regression C

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	-1.8683				
Ln(AO-Al)	0.3419	0.0451	7.58	0.000	0.8293
Ln(DC-Fe)	0.4070	0.0554	7.35	0.000	0.8981
pH-$CaCl_2$	-0.3119	0.1109	-2.81	0.006	0.9076
R^2 = 0.91	S.E.† = 0.1941	EDF‡ = 77	F = 252.04	P = 0.000	

† Standard Error of the Estimate (Ln units)
‡ Error Degrees of Freedom

detected or removed. One equation contained only a single predictor variable, Ln(DC-Al), with an r^2 of 0.87. The simplicity of this equation reflects the basic similarity in chemical and physical properties of these soils, with sulfate adsorption in subsurface horizons depending largely on Al concentration. Other equations incorporated combinations of AO-Al, Cr-Fe, DC-Fe, and pH-$CaCl_2$ as predictors, with some improvement in R^2 values. Standard errors of all equations were similar, varying from the equivalent of 1.3 mg S kg^{-1} for the simplest model to 1.2 mg S kg^{-1} for the most complex model. Choice of a prediction equation would be based on soil analytical data available.

Results of correlation analyses suggested a second grouping of soils into mesic zone and frigid zone soils. Regression equations developed for mesic zone soils are presented in Table 7.6. Outliers removed from mesic zone regression A were 4480, 6150, and 6160. In this equation, predictors positively related to sulfate adsorption included exchangeable Al and AO-Fe. Predictors negatively influencing sulfate adsorption were pH-$CaCl_2$ and extractable P. Standardized parameter estimates indicated that exchangeable Al (0.461) and pH-$CaCl_2$ (-0.474) were most important in determining sulfate adsorption, while extractable P (-0.327) and AO-Fe (0.290) were important modifying influences. The relationship between sulfate adsorption predicted by regression A and actual sulfate adsorption in mesic zone soils is portrayed in Figure 7.1.

Table 7.6

Regressions for Mesic Zone Soils Subsurface Horizons

Mesic Zone Regression A

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	0.4896				
Ln(Ex-Al+1)	0.2138	0.0467	4.57	0.000	0.6311
pH-$CaCl_2$	-0.2997	0.0671	-4.47	0.000	0.6818
Ln(Ext-P)	-0.2341	0.0469	-4.99	0.000	0.7605
Ln(AO-Fe)	0.4115	0.0835	4.93	0.000	0.8330
R^2 = 0.83	S.E.† = 0.3096	EDF‡ = 56	F = 69.81	P = 0.000	

Mesic Zone Regression B

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	5.8998				
Ln(Ex-Al+1)	0.2051	0.0576	3.56	0.001	0.6435
Ln(Org-C)	-0.2208	0.0682	-3.24	0.002	0.6489
Ln(ΣBases+1)	0.4886	0.1049	4.66	0.000	0.6504
pH-H_2O	-0.6196	0.1006	-6.16	0.000	0.7887
R^2 = 0.79	S.E.† = 0.3685	EDF‡ = 58	F = 54.11	P = 0.000	

† Standard Error of the Estimate (Ln units)
‡ Error Degrees of Freedom

Table 7.6 (continued)

Mesic Zone Regression C

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	2.6825				
pH-H_2O	-0.3013	0.0484	-6.22	0.000	0.6775
Ln(%Clay)	0.5230	0.0897	5.83	0.000	0.8035
R^2 = 0.80	S.E.† = 0.3255	EDF‡ = 53	F = 108.39	P = 0.000	

Mesic Zone Regression D

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	2.9053				
pH-H_2O	-0.2016	0.0635	-3.17	0.003	0.6775
Ln(%Clay)	0.6013	0.0920	6.54	0.000	0.8035
Ln(Org-C)	-0.1943	0.0627	-3.10	0.003	0.8221
Ln(Ex-Al+1)	0.1452	0.0503	2.89	0.006	0.8471
R^2 = 0.85	S.E.† = 0.2927	EDF‡ = 51	F = 70.64	P = 0.000	

† Standard Error of the Estimate (Ln units)
‡ Error Degrees of Freedom

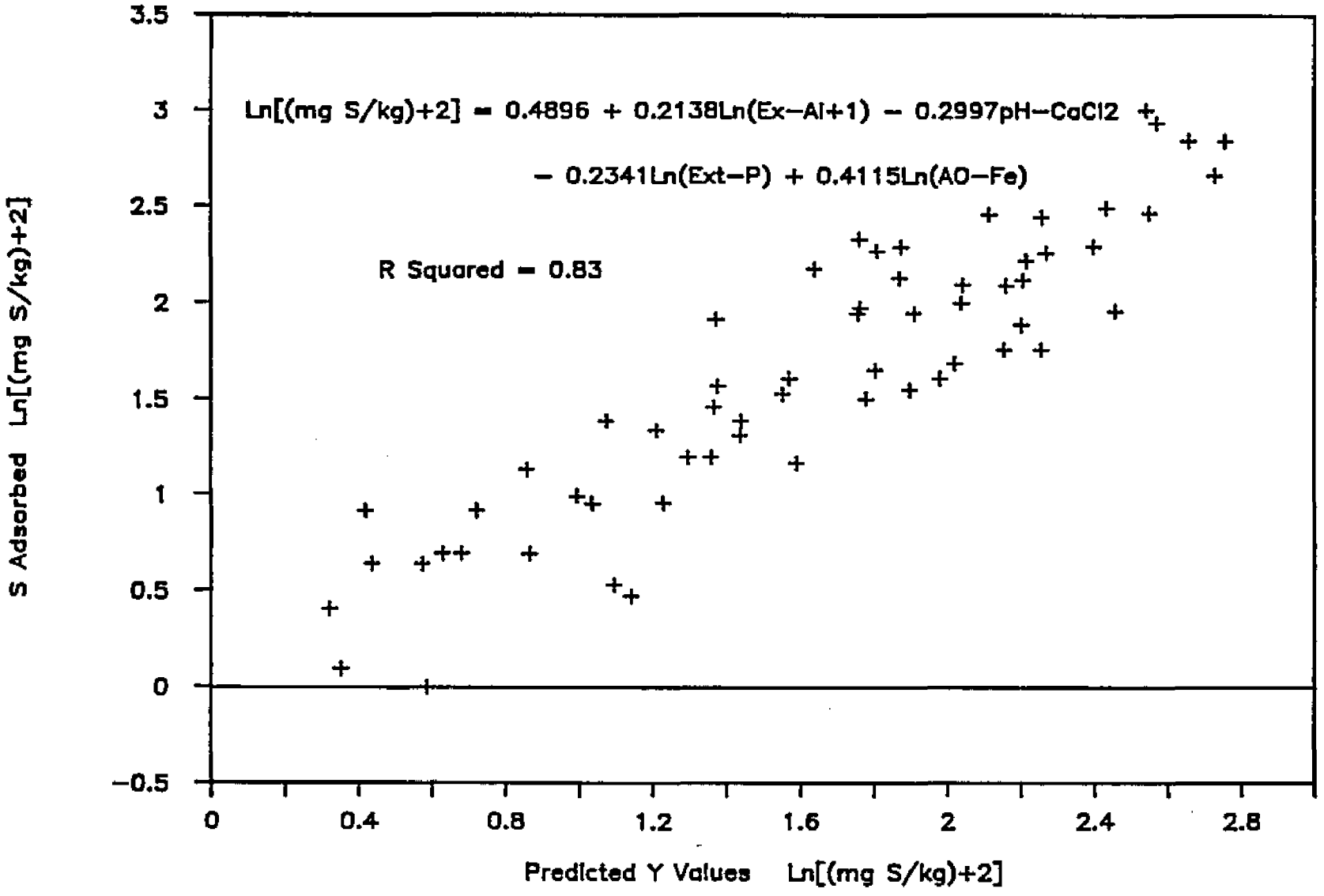

Figure 7.1

Mesic Zone Soils - Regression A Results

Mesic zone regressions B, C, and D (Table 7.6) were developed to allow estimation of sulfate adsorption using exchangeable Al, organic carbon, pH-H_2O, % clay, and sum of bases as predictors. Outlier 4480 was removed from regression B, while 4480, 4520, 4530, 4540, 4550, 4560, 6150, and 6160 were removed from regressions C and D.

Regression equations developed from combined frigid zone soils data are presented in Table 7.7. Only one outlier was removed, 3550. Equations involved combinations of DC-Al and pH-$CaCl_2$; AO-Al, pH-$CaCl_2$, and Cr-Fe; or exchangeable Al, DC-Fe, and pH-H_2O. Effects of Al and Fe fractions were positive and those of pH negative. R^2 values (0.86-0.89) and standard errors of the estimate (approximately 1.3 mg S kg^{-1}) were comparable to those obtained for regressions developed for Grayling, Rubicon, and Kalkaska series combined (Table 7.5), suggesting that grouping all frigid zone soil series together is appropriate. Results presented in Chapter V also indicated patterns of sulfate adsorption in Montcalm soils were similar to those in other frigid zone soils. The relationship between predicted sulfate adsorption and actual sulfate adsorption described by regression equation A (Table 7.7) is depicted in Figure 7.2.

Regression equations developed for individual soil series are presented in Tables 7.8 to 7.12. Data from the two "Block 7" pedons were included in Grayling and Montcalm series data sets for regression purposes, although these

Table 7.7

Regressions for Frigid Zone Soils Subsurface Horizons

Frigid Zone Soils Regression A

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	-1.0843				
Ln(DC-Al)	0.5897	0.0255	23.16	0.000	0.8470
pH-$CaCl_2$	-0.1647	0.0267	-6.18	0.000	0.8854
R^2 = 0.89	S.E.† = 0.2219	EDF‡ = 114	F = 440.23	P = 0.000	

Frigid Zone Soils Regression B

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	-1.9316				
Ln(AO-Al)	0.4564	0.0290	15.75	0.000	0.8171
pH-$CaCl_2$	-0.2043	0.0306	-6.67	0.000	0.8409
Ln(Cr-Fe)	0.2514	0.0415	6.06	0.000	0.8799
R^2 = 0.88	S.E.† = 0.2282	EDF‡ = 113	F = 275.95	P = 0.000	

Frigid Zone Soils Regression C

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	-1.0397				
Ln(Ex-Al+1)	0.1992	0.0357	5.58	0.000	0.7247
Ln(DC-Fe)	0.4742	0.0464	10.23	0.000	0.8368
pH-H_2O	-0.1888	0.0449	-4.21	0.000	0.8589
R^2 = 0.86	S.E.† = 0.2473	EDF‡ = 113	F = 229.25	P = 0.000	

† Standard Error of the Estimate (Ln units)
‡ Error Degrees of Freedom

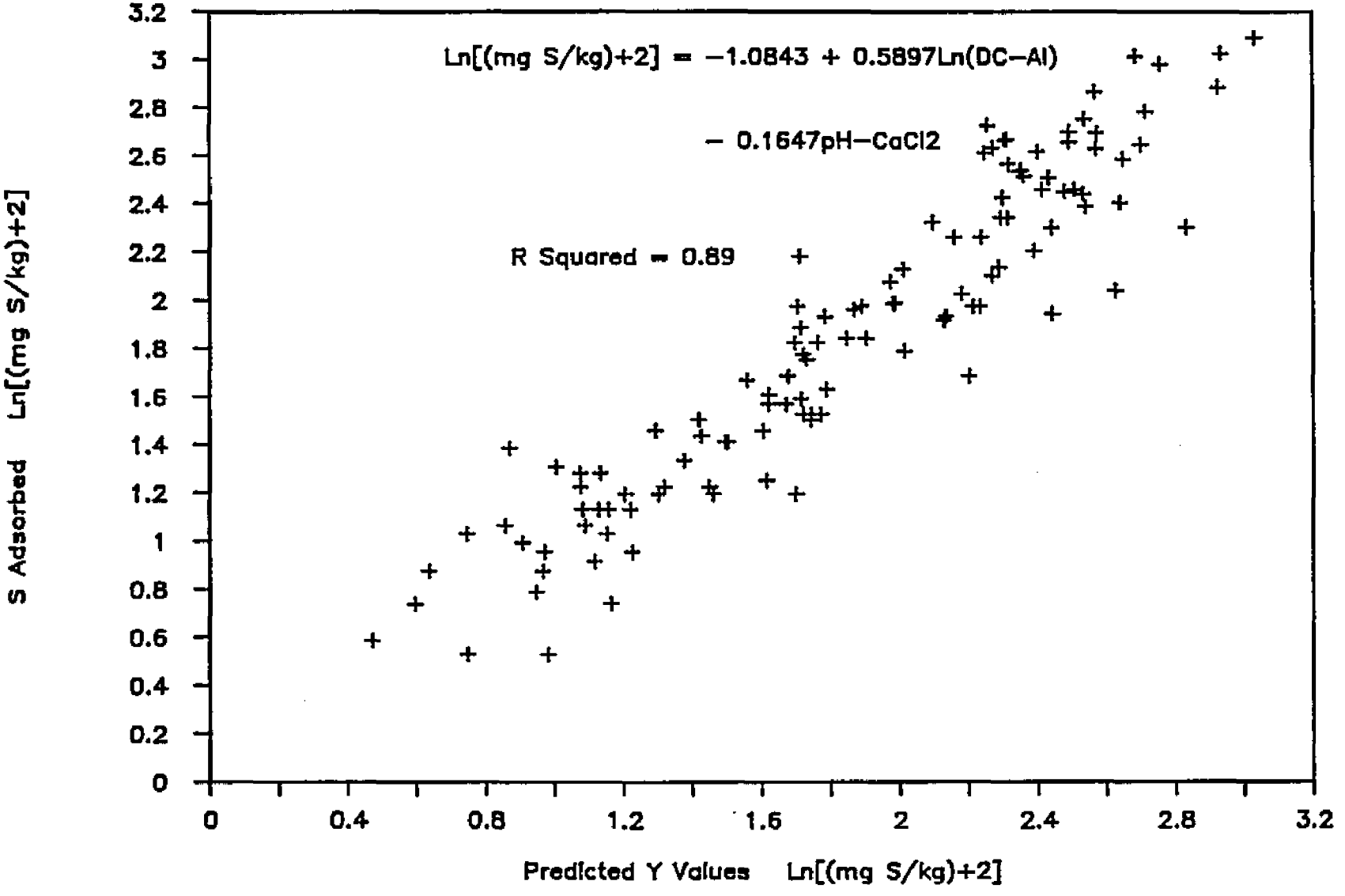

Figure 7.2

Frigid Zone Soils - Regression A Results

pedons deviated from typical series characteristics. No outliers were removed from Grayling, Rubicon, or Kalkaska data sets. One outlier, 3550, was removed from Montcalm data. Data for samples 6150 and 6160 were removed from Spinks series regressions, while sample 4480 data were removed from Oshtemo series regressions.

Regressions for Grayling and Rubicon were similar in that predictors included measures of extractable Al in combination with pH-H_2O (Table 7.8). The effect of pH in these equations was positive, pH apparently correcting for over-prediction of sulfate adsorption by Al at lower pH values. These equations have predictive value, but should not be misconstrued as evidence for enhancement of sulfate adsorption by increasing pH. Deletion of pH as a predictor from either equation would not greatly reduce usefulness of the equations. Sulfate adsorption in the Kalkaska series was predicted by DC-Al or by combinations of DC-Al and AO-Fe or AO-Al and DC-Fe (Table 7.9). Inclusion of variables based on Fe may reflect the increasing importance of Fe in sulfate adsorption in more highly podzolized soils such as Kalkaska.

Prediction of sulfate adsorption in the Montcalm series relied on use of DC-Al in combination with pH-$CaCl_2$, pH-H_2O, or sum of base cations (Table 7.10). In the Montcalm series, pH and base status influences were negative, reflecting the increasing importance of pH control over sulfate adsorption in Alfisols. Regression equations

Table 7.8

Regressions for Grayling and Rubicon Subsurface Horizons

Grayling

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	-1.3440				
Ln(Ex-Al+1)	0.6127	0.0392	15.62	0.000	0.9183
pH-H_2O	0.3211	0.0960	3.34	0.003	0.9436

R^2 = 0.94 S.E.† = 0.1593 EDF‡ = 25 F = 208.99 P = 0.000

Rubicon

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	-5.9217				
Ln(DC-Al)	0.8396	0.0496	16.93	0.000	0.8865
pH-H_2O	0.4760	0.1091	4.36	0.000	0.9391

R^2 = 0.94 S.E.† = 0.1693 EDF‡ = 22 F = 169.74 P = 0.000

† Standard Error of the Estimate (Ln units)
‡ Error Degrees of Freedom

Table 7.9

Regressions for Kalkaska Subsurface Horizons

Kalkaska Regression A

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	-1.9990				
Ln(DC-Al)	0.6016	0.0417	14.42	0.000	0.8888

R^2 = 0.89 S.E.† = 0.2036 EDF‡ = 26 F = 207.81 P = 0.000

Kalkaska Regression B

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	-1.8754				
Ln(DC-Al)	0.3363	0.0849	3.96	0.001	0.8888
Ln(AO-Fe)	0.2569	0.0749	3.43	0.002	0.9244

R^2 = 0.92 S.E.† = 0.1712 EDF‡ = 25 F = 152.81 P = 0.000

Kalkaska Regression C

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	-3.5414				
Ln(AO-Al)	0.3554	0.0553	6.43	0.000	0.8656
Ln(DC-Fe)	0.4138	0.0821	5.04	0.000	0.9333

R^2 = 0.93 S.E.† = 0.1608 EDF‡ = 25 F = 175.03 P = 0.000

† Standard Error of the Estimate (Ln units)
‡ Error Degrees of Freedom

Table 7.10

Regressions for Montcalm Subsurface Horizons

Montcalm Regression A

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	-0.6887				
Ln(DC-Al)	0.5213	0.0435	11.99	0.000	0.8370
pH-$CaCl_2$	-0.1651	0.0302	-5.46	0.000	0.9143
R^2 = 0.91	S.E.† = 0.2035	EDF‡ = 33	F = 176.13	P = 0.000	

Montcalm Regression B

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	-0.1809				
Ln(DC-Al)	0.4867	0.0463	10.51	0.000	0.8370
pH-H_2O	-0.1858	0.0330	-5.62	0.000	0.9167
R^2 = 0.92	S.E.† = 0.2007	EDF‡ = 33	F = 181.66	P = 0.000	

Montcalm Regression C

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	-1.8527				
Ln(DC-Al)	0.5940	0.0370	16.06	0.000	0.8370
Ln(ΣBases+1)	-0.1903	0.0334	-5.70	0.000	0.9179
R^2 = 0.92	S.E.† = 0.1993	EDF‡ = 33	F = 184.38	P = 0.000	

† Standard Error of the Estimate (Ln units)
‡ Error Degrees of Freedom

developed for the Spinks series were somewhat similar to those developed for the Montcalm series in that a measure of pH was included in all equations, pH being important in combination with DC-Al or % clay (Table 7.11). Extractable SO_4-S was also significantly related to sulfate adsorption in the Spinks series, past sulfate retention under field conditions serving as a positive predictor for sulfate adsorption under laboratory conditions.

Sulfate adsorption in the Oshtemo series was consistently predicted by a combination of exchangeable Al and extractable P, variously modified by pH-H_2O, % clay, Cr-Fe, AO-Al, and DC-Al (Table 7.12). Al, clay, and Fe exhibited positive influences on sulfate adsorption, while pH and extractable P exerted negative influences. The negative effect of extractable P arises from the strong competition by P for adsorption sites. High extractable P concentrations in certain Oshtemo pedons were related to past cultivation or grazing producing increased levels of P in these soils. Similar forest soils subject to earlier agricultural disturbance may likewise have reduced sulfate adsorption capacities.

R^2 values of individual series regression equations were higher than R^2 values of equations developed for groups of series. As compared to frigid zone soils, R^2 values were lower and standard errors of the estimate higher for mesic zone soils, reflecting greater variability in soil properties of mesic series. Maximum R^2 values for series

Table 7.11

Regressions for Spinks Subsurface Horizons

Spinks Regression A

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	-2.3608				
Ln(DC-Al)	0.8039	0.1321	6.08	0.000	0.7873
pH-$CaCl_2$	-0.1701	0.0725	-2.35	0.027	0.8257
R^2 = 0.83	S.E.† = 0.3210	EDF‡ = 25	F = 59.20	P = 0.000	

Spinks Regression B

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	2.6758				
Ln(% Clay)	0.6023	0.1233	4.89	0.000	0.6150
pH-H_2O	-0.3160	0.0625	-5.06	0.000	0.8097
R^2 = 0.81	S.E.† = 0.3353	EDF‡ = 25	F = 53.18	P = 0.000	

Spinks Regression C

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	2.3892				
Ln(% Clay)	0.3886	0.1333	2.91	0.008	0.6150
pH-H_2O	-0.2511	0.0600	-4.18	0.000	0.8097
Ln(Ext-S)	0.2531	0.0905	2.80	0.010	0.8565
R^2 = 0.86	S.E.† = 0.2972	EDF‡ = 24	F = 47.73	P = 0.000	

† Standard Error of the Estimate (Ln units)
‡ Error Degrees of Freedom

Table 7.12

Regressions for Oshtemo Subsurface Horizons

Oshtemo Regression A

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	3.4421				
pH-H_2O	-0.2800	0.0812	-3.45	0.002	0.6452
Ln(Ext-P)	-0.2878	0.0597	-4.82	0.000	0.7393
Ln(Ex-Al+1)	0.2779	0.0585	4.75	0.000	0.8533

R^2 = 0.85 S.E.† = 0.2957 EDF‡ = 29 F = 56.25 P = 0.000

Oshtemo Regression B

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	0.9188				
Ln(% Clay)	0.3745	0.1081	3.47	0.002	0.4767
Ln(Ex-Al+1)	0.3507	0.0434	8.08	0.000	0.7353
Ln(Ext-P)	-0.2893	0.0597	-4.85	0.000	0.8538

R^2 = 0.85 S.E.† = 0.2952 EDF‡ = 29 F = 56.46 P = 0.000

Oshtemo Regression C

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	-2.0892				
Ln(Ex-Al+1)	0.3896	0.0365	10.67	0.000	0.6993
Ln(Cr-Fe)	0.4098	0.1077	3.80	0.001	0.7938
Ln(Ext-P)	-0.2190	0.0578	-3.79	0.001	0.8621

R^2 = 0.86 S.E.† = 0.2867 EDF‡ = 29 F = 60.42 P = 0.000

Table 7.12 (continued)

Oshtemo Regression D

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	-0.8278				
Ln(AO-A1)	0.4256	0.0986	4.32	0.000	0.4586
Ln(Ex-A1+1)	0.3356	0.0404	8.30	0.000	0.7222
Ln(Ext-P)	-0.3471	0.0587	-5.92	0.000	0.8742

R^2 = 0.87 S.E.† = 0.2739 EDF‡ = 29 F = 67.16 P = 0.000

Oshtemo Regression E

Predictor Variable	Parameter Estimate	Standard Error	t-Value (b=0)	P (b=0)	Sequential R^2
Constant	-1.1878				
Ln(DC-A1)	0.4446	0.1026	4.33	0.000	0.4852
Ln(Ex-A1+1)	0.3465	0.0389	8.90	0.000	0.7507
Ln(Ext-P)	-0.2958	0.0553	-5.35	0.000	0.8745

R^2 = 0.87 S.E.† = 0.2736 EDF‡ = 29 F = 67.34 P = 0.000

† Standard Error of the Estimate (Ln units)
‡ Error Degrees of Freedom

regressions ranged from 0.94 to 0.86, suggesting an inherent variability on the order of 6 to 14% in sulfate adsorption determinations. This range brackets the coefficient of variation of 10.1% determined for bulk sample sulfate adsorption (Appendix C).

LINEAR DISCRIMINANT FUNCTIONS

An alternative to prediction of sulfate adsorption using regression equations is the use of linear discriminant functions to classify soils. The examples presented here were developed to classify entire pedons as to sulfate adsorbing ability based on S adsorbed per square meter in the upper 150 cm of sulfate adsorbing horizons (g S m^{-2}). Content of S adsorbed on a pedon basis was calculated from S adsorbed (mg S kg^{-1}), horizon thickness (cm), and bulk density (g cm^{-3}). Pedons were then divided into groups of low (4.0 to 9.5 g S m^{-2}), medium (11.0 to 15.1 g S m^{-2}), and high (15.9 to 21.1 g S m^{-2}) sulfate adsorption. Group means are presented in Table 7.13.

Two pedons that exhibited anomalous sulfate adsorption characteristics, Spinks Block I and Oshtemo Block V, were excluded from development of discriminant functions but were subsequently classified. Soil chemical properties to be tested for use as discriminant variables were converted to contents in g m^{-2} to 150 cm in sulfate adsorbing horizons in the same way as sulfate adsorption data. Soil pH was converted to meq H^+ m^{-2}, assuming H^+ concentration could be

calculated from pH measured in solution and using mL H_2O g^{-1} soil as a dilution factor to calculate H^+ concentration in soils.

Table 7.13

Mean Sulfate Adsorption in Pedons by Discriminant Group

Group	n	Mean†	Standard Deviation
		------- g S m^{-2} -------	
Low	18	7.4	1.5
Medium	12	12.8	1.2
High	6	18.5	2.2

† Mean based on amount of S adsorbed calculated for upper 150 cm of sulfate adsorbing horizons

Selection of discriminant variables was based on minimizing Wilk's Lambda, a criterion based on the overall multivariate F ratio for testing differences among group centroids. A variable which maximizes the F ratio also minimizes Wilk's Lambda, thus the lower the Wilk's Lambda the higher the discriminating power present. In an univariate case, Wilk's Lambda is equivalent to $1-r^2$ (Hintze, 1985). One set of discriminant coefficients was calculated for each sulfate adsorption group. For each function, raw data vectors are multiplied by the vector of discriminant coefficients, and the results are summed together with the constant. The unknown case is classified into the group whose function gives the highest score, in

effect assigning the case to the group for which it has the highest probability of membership (Hintze, 1985) given its vector of soil properties.

Results of discriminant analyses are presented in Table 7.14. In discriminant function A, significant variables included DC-Fe, DC-Al, organic carbon, and $H^+(CaCl_2)$, all calculated on a content basis as described. When applied to pedon data used to develop the function, 83.3% of pedons were correctly classified into sulfate adsorption categories. All pedons in the low sulfate adsorption group were correctly classified. Least accurate classification was for the medium sulfate adsorption group where 5 of 12 pedons were mis-classified in the low group. In the high sulfate adsorption group, 1 of 6 pedons was mis-classified in the medium sulfate adsorption group. These results suggest that the discriminant function is conservative in that it tends to assign soils to groups with lower than actual sulfate adsorption abilities. Both pedons not included in development of the discriminant function (Spinks Block I, Oshtemo Block V) were classified in the low group, a classification which correctly summarized their weak sulfate retentive abilities.

Initial grouping of pedons on the basis of g S adsorbed per m^2 to 150 cm did not follow series groupings. Spinks, Oshtemo, and Montcalm pedons occurred in low, medium, and high adsorption groups. Grayling, Rubicon, and Kalkaska pedons occurred in low and medium groups, with no definite

Table 7.14

Sulfate Adsorption Discriminant Functions

Discriminant Function A

Variable†	-Sulfate Adsorption Group- Low	Medium	High	R^2-Del‡	F	P
	-- Discriminant Coefficients --					
Constant	1.692001	0.059171	-0.751171			
DC-Fe	0.000012	-0.000037	0.000025	0.181	3.3	0.049
DC-Al	-0.001226	0.000816	0.000411	0.513	15.8	0.000
Org-C	0.000206	-0.000171	-0.000035	0.228	4.4	0.020
H^+-$CaCl_2$	-0.001388	-0.001274	0.002661	0.308	6.7	0.004

Overall Wilk's Lambda = 0.159 % Mis-classified = 16.7

Discriminant Function B

Variable†	-Sulfate Adsorption Group- Low	Medium	High	R^2-Del‡	F	P
	-- Discriminant Coefficients --					
Constant	1.626378	0.042134	-0.668512			
AO-Fe	-0.000165	-0.000069	0.000233	0.488	14.8	0.000
AO-Al	-0.000329	0.000228	0.000101	0.439	12.1	0.000
H^+-$CaCl_2$	-0.002214	-0.000396	0.002610	0.342	8.0	0.002

Overall Wilk's Lambda = 0.167 % Mis-classified = 19.4

Discriminant Function C

Variable†	-Sulfate Adsorption Group- Low	Medium	High	R^2-Del‡	F	P
	-- Discriminant Coefficients --					
Constant	1.525738	0.015234	-0.540973			
AO-Fe	-0.000201	-0.000047	0.000248	0.554	19.3	0.000
AO-Al	-0.000313	0.000243	0.000070	0.354	8.5	0.001
Ex-Al	-0.002215	-0.001747	0.003962	0.329	7.6	0.002

Overall Wilk's Lambda = 0.170 % Mis-classified = 19.4

† Fe, Al, C in g m^{-2} and H^+ in meq m^{-2} to depth of 150 cm
‡ Increase in Wilk's Lambda if variable were removed

patterns between series discernible. This result suggests that classification of a single pedon is not only insufficient but would be misleading if used to characterize an entire soil series as to sulfate adsorption ability. Classification of multiple pedons would be required to establish any pattern or lack thereof.

Discriminant functions (B, C) were also developed based on AO-Al and AO-Fe contents in combination with $H^+(CaCl_2)$ or exchangeable Al (Table 7.14). These functions behaved similarly to function A, although correct classification was somewhat lower (80.6%). Classification was again conservative, mis-classification placing pedons into lower adsorption groups than actual.

Preliminary results indicate that the use of linear discriminant functions to classify individual pedons as to relative sulfate adsorption abilities holds some promise. Expansion of the data base to include more pedons with medium and high adsorptive capacities would probably improve discriminating power. Further refinement would incorporate probabilities of class membership, which are presently unknown but have been assumed to be equal in the examples discussed.

SUMMARY AND CONCLUSIONS

Results of regression analyses indicated that sulfate adsorption in representative Michigan forest soils was predictable using relatively few predictor variables derived

from commonly measured soil properties. Maximum regression R^2 values ranged from 0.85 to 0.94, depending on grouping of soils and specific predictors employed. The strongest, most consistent predictors were extractable Al fractions (DC-Al, AO-Al) and exchangeable Al. Additional consistently significant predictors were extractable Fe fractions (DC-Fe, AO-Fe, Cr-Fe), and both measures of pH (H_2O, $CaCl_2$). Other variables that contributed to prediction in certain cases included % clay, organic carbon, extractable P, and extractable SO_4-S. The regression equations presented, or similar ones tailored to meet specific data availabilities, should prove useful in predicting sulfate adsorption in other similar forest soils.

Linear discriminant functions hold promise in classification of pedons into groups based on calculated sulfate adsorptive capacities in the upper 150 cm of sulfate adsorbing horizons. Variables with discriminating power included dithionite-citrate extractable Fe and Al, organic carbon, $H^+(CaCl_2)$, ammonium oxalate extractable Fe and Al, and exchangeable Al, all calculated on a content basis for the upper 150 cm of sulfate adsorbing horizons. Expansion of the present data base to include more pedons with medium and high adsorptive capacities would improve discriminating power.

Chapter VIII

PREDICTION OF SULFATE ADSORPTION IN MICHIGAN FOREST SOILS USING EXISTING SOIL CHARACTERIZATION DATA

This chapter examines the use of regression equations presented in Chapter VII to predict sulfate adsorption in selected Michigan forest soils using existing soil characterization data (SCS-USDA, 1980; MTU-FFC, 1982-1984). Soil characterization data were obtained from published reports of soil analyses performed as part of the Michigan soil survey program. Laboratory analyses for soils sampled prior to 1978 were performed by USDA Soil Survey Laboratories in Lincoln, Nebraska and Beltsville, Maryland (SCS-USDA, 1980). Laboratory analyses for soils sampled from 1978 on were performed by the Michigan Technological University Soil Survey Laboratory (MTU-FFC, 1982-1984). Field work and laboratory analyses were conducted in cooperation with the Michigan Agricultural Experiment Station (SCS-USDA, 1980), Michigan Department of Agriculture (MTU-FFC, 1982-1984), and the Soil Conservation Service, United States Department of Agriculture. Data selected from these sources will subsequently be referred to as SCS/MTU soil characterization data.

The results presented here are not an exhaustive attempt to predict sulfate adsorption in all Michigan soil series described in published soil characterization data

reports. Due to high variability in sulfate adsorption within series, discussed in Chapter V, prediction was attempted only for series with analytical data for three or more pedons. In addition, only series considered potentially sensitive to acid deposition (Appendix A) and important as forest soils were considered. Fifteen series met these qualifications and were used for predictive purposes. Two groups composed of closely related mesic zone series, Alfic Udipsamments and coarse-loamy Hapludalfs, were also included because data on mesic zone series were limited. Prediction equations were applied separately to mesic zone and frigid zone series. Predicted values have been converted to the scale of original measurement, which can be used as a relative measure of sulfate adsorption for comparisons with predicted values for other soils, but which underestimates actual values because regression equations were based on logarithmically transformed variables.

FRIGID ZONE SOIL SERIES

Predicted sulfate adsorption in subsurface horizons of frigid zone series is presented in Tables 8.1, 8.2, and 8.3. Equations applicable to frigid zone series, within constraints of data availability, were frigid zone regressions A and C (Table 7.7), entic-spodic regression A (Table 7.5), and series-specific regressions for Grayling (Table 7.8), Rubicon (Table 7.8), Kalkaska (Table 7.9, regression A), and Montcalm (Table 7.10, regressions B,C).

Predicted sulfate adsorption abilities in frigid zone Udipsamments and Haplorthods (Table 8.1) were similar, being highest in upper B horizons and decreasing with depth. Within the Grayling and Croswell series, all regressions predicted similar adsorption. In the Rubicon series, the series-specific regression (Table 7.8) predicted substantially higher sulfate adsorption than other regression equations, because of higher DC-Al concentrations in the Rubicon soils sampled for SCS/MTU soil characterization studies compared to the soils used to develop the equation. In the Kalkaska series, frigid zone regression C (Table 7.7) predicted higher sulfate adsorption than other equations, evidently due to the influence of additional, more strongly podzolized pedons included by use of this equation.

In frigid zone Alfic Udipsamments, Eutric Glossoboralfs, and Typic Eutroboralfs (Table 8.2), all regressions based on DC-Al predicted similar levels of sulfate adsorption. Frigid zone regression C (Table 7.7), based on exchangeable Al, DC-Fe, and pH-H_2O, tended to predict higher adsorption. Montcalm series regressions B and C (Table 7.10) were also applied to the Graycalm, Pemene, and Emmet series because of morphological and soil chemical similarities between series. Montcalm regression A (Table 7.10), based on DC-Al and pH-$CaCl_2$, produced estimates (not presented) similar to those calculated from regressions B and C. Predicted sulfate adsorption in all

Table 8.1

Predicted Sulfate Adsorption in the

Grayling, Croswell, Rubicon, and Kalkaska Series

Grayling (mixed, frigid Typic Udipsamments)

Soil[1] Hor.	FZR-A[2] Mean[†]	SD[‡]	n	FZR-C[3] Mean	SD	n	ESR-A[4] Mean	SD	n	SSR[5] Mean	SD	n
Bw1	14.0	2.9	6	13.5	4.2	8	15.3	3.7	6	17.2	3.6	9
Bw2	10.8	3.8	5	10.5	1.9	7	11.8	4.3	5	12.5	2.4	8
BC	7.1	0.1	2	4.4	3.0	4	7.6	0.0	2	6.8	2.3	8
C	0.2	-	1	2.8	1.1	3	0.1	-	1	4.7	3.5	9

Croswell (sandy, mixed, frigid Entic Haplorthods)

Soil[1] Hor.	FZR-A[2] Mean	SD	n	FZR-C[3] Mean	SD	n	ESR-A[4] Mean	SD	n	SSR[5] Mean	SD	n
Bs1	15.5	2.6	3	19.2	11.9	3	17.5	4.4	3			
Bs2	12.6	8.8	2	8.8	8.1	2	14.7	10.0	2	N.A.[6]		
BC	6.4	0.5	2	6.6	2.3	2	7.6	0.0	2			

Rubicon (sandy, mixed, frigid Entic Haplorthods)

Soil[1] Hor.	FZR-A[2] Mean	SD	n	FZR-C[3] Mean	SD	n	ESR-A[4] Mean	SD	n	SSR[5] Mean	SD	n
Bs1	17.3	2.6	4	15.2	3.6	6	19.8	2.4	4	28.9	1.4	4
Bs2	12.4	2.4	4	8.5	4.2	6	14.2	2.3	4	21.0	3.4	4
BC	6.4	0.5	3	5.1	3.4	5	7.6	0.0	3	11.0	3.4	3
C	6.2	-	1	3.0	1.1	3	7.6	-	1	14.9	-	1

Kalkaska (sandy, mixed, frigid Typic Haplorthods)

Soil[1] Hor.	FZR-A[2] Mean	SD	n	FZR-C[3] Mean	SD	n	ESR-A[4] Mean	SD	n	SSR[5] Mean	SD	n
Bh	15.0	1.9	3	24.8	8.0	8	14.6	2.7	3	12.3	2.1	3
Bs	17.6	1.6	3	15.6	5.3	8	19.1	2.4	3	15.8	1.8	3
BC	9.8	2.5	2	9.1	4.1	7	10.4	3.9	2	8.8	3.2	2
C	-	-	-	5.8	1.6	5	-	-	-	-	-	-

1 Soil Horizon
2 Frigid Zone Regression A
3 Frigid Zone Regression C
4 Entic-Spodic Regression A
5 Series Specific Regression
6 Not Applicable
† Mean, ‡ Standard Deviation in mg S kg^{-1}

Table 8.2

Predicted Sulfate Adsorption in the

Graycalm, Montcalm, Pemene, and Emmet Series

Graycalm (mixed, frigid, Alfic Udipsamments)

Soil[1] Hor.	FZR-A[2] Mean†	SD‡	n	FZR-C[3] Mean	SD	n	MTR-B[4] Mean	SD	n	MTR-C[5] Mean	SD	n
Bw1	7.3	4.9	4	16.4	2.3	4	7.9	4.4	4	6.5	4.9	4
Bw2	9.0	2.4	4	15.6	3.1	4	9.4	1.8	4	8.2	2.8	4
Bw3	6.0	3.7	4	12.3	2.8	4	6.6	3.5	4	5.4	3.4	4
E!	0.5	0.1	3	6.6	1.6	3	1.3	0.2	3	0.3	0.0	3
E'2	0.4	0.1	2	5.9	1.4	2	1.2	0.2	2	0.3	0.0	2
Bt	2.7	4.4	2	7.2	-	1	3.0	4.2	2	4.4	-	1

Montcalm (coarse-loamy, mixed, frigid Eutric Glossoboralfs)

Soil[1] Hor.	FZR-A[2] Mean	SD	n	FZR-C[3] Mean	SD	n	MTR-B[4] Mean	SD	n	MTR-C[5] Mean	SD	n
Bw1	15.0	4.7	3	19.2	8.0	3	13.4	4.1	3	13.6	3.7	3
Bw2	9.0	3.1	3	13.1	5.3	3	8.5	3.2	3	8.3	2.5	3

Pemene (coarse-loamy, mixed, frigid Eutric Glossoboralfs)

Soil[1] Hor.	FZR-A[2] Mean	SD	n	FZR-C[3] Mean	SD	n	MTR-B[4] Mean	SD	n	MTR-C[5] Mean	SD	n
Bw1	11.6	4.0	4	9.1	6.4	4	9.9	2.6	4	10.2	3.7	4
E/B	7.9	3.1	4	8.8	4.7	4	7.2	2.4	4	7.5	2.4	4
B/E	5.8	-	1	3.8	-	1	5.9	-	1	5.6	-	1
Bt	8.6	2.1	2	4.8	1.8	2	6.8	0.9	2	7.6	0.1	2
BC	3.8	-	1	1.5	-	1	3.5	-	1	4.4	-	1

1 Soil Horizon
2 Frigid Zone Regression A
3 Frigid Zone Regression C
4 Montcalm Regression B
5 Montcalm Regression C
† Mean, ‡ Standard Deviation in mg S kg^{-1}

Table 8.2 (continued)

Emmet (coarse-loamy, mixed, frigid Typic Eutroboralfs)

Soil[1] Hor.	FZR-A[2] Mean†	SD‡	n	FZR-C[3] Mean	SD	n	MTR-B[4] Mean	SD	n	MTR-C[5] Mean	SD	n
Bw1	9.8	2.3	5	14.0	7.2	5	8.9	2.2	5	8.5	1.7	5
Bw2	5.9	0.1	2	9.2	5.0	2	5.8	0.3	2	5.8	0.0	2
E'	3.3	4.8	2	9.8	10.1	2	3.2	4.2	2	3.0	4.0	2
E/B	10.7	-	1	15.9	-	1	9.7	-	1	8.7	-	1
Bt	8.6	-	1	4.3	-	1	6.7	-	1	6.6	-	1
BC	4.5	-	1	1.6	-	1	3.7	-	1	3.6	-	1

1 Soil Horizon
2 Frigid Zone Regression A
3 Frigid Zone Regression C
4 Montcalm Regression B
5 Montcalm Regression C
† Mean, ‡ Standard Deviation in mg S kg^{-1}

four series was highest in upper B horizons, decreased with depth, and increased slightly in Bt horizons.

Inclusion of Fragiorthods (Table 8.3) in prediction of sulfate adsorption is an extrapolation, as Fragiorthods were not included in soils sampled for development of regression equations. Fragiorthods occur extensively in the upper peninsula of Michigan and their relative sensitivity to acid deposition is of importance. If relationships between soil properties and sulfate adsorption developed for northern lower peninsula soils hold true, it appears that Fragiorthods have substantial abilities to adsorb sulfate throughout the solum. As previously noted for other frigid zone soils, frigid zone regression C, based on exchangeable Al and DC-Fe, predicted substantially higher sulfate adsorption in Fragiorthods than frigid zone regression A, which is based on DC-Al concentration.

An overall comparison of predicted sulfate adsorption for frigid zone soils suggests that Alfic Udipsamments, Eutric Glossoboralfs, and Typic Eutroboralfs (Table 8.2) have the lowest sulfate adsorbing abilities, while Typic Udipsamments, Entic Haplorthods, and moderately developed Typic Haplorthods (Table 8.1) have moderate abilities to adsorb sulfate. Strongly developed Typic Haplorthods (Table 8.1, regression FZR-C) and Fragiorthods (Table 8.3) have the strongest ability to adsorb sulfate, apparently due to greater acidity, higher levels of exchangeable Al, and greater sesquioxide concentrations in upper B horizons.

Table 8.3

Predicted Sulfate Adsorption in the

Yalmer, Munising, and Champion Series

Yalmer (sandy, mixed, frigid Alfic Fragiorthods)

Soil[1] Hor.	-- FZR-A[2] -- Mean†	SD‡	n	-- FZR-C[3] -- Mean	SD	n
Bh	22.1	8.7	3	32.0	11.7	5
Bs	19.6	3.0	3	23.6	2.9	4
2E/Bx	-	-	-	9.6	1.0	3
2B/Ex	-	-	-	8.4	0.8	2
2Bt	-	-	-	16.7	-	1
2C	-	-	-	11.0	-	1

Munising (coarse-loamy, mixed, frigid Alfic Fragiorthods)

Soil[1] Hor.	-- FZR-A[2] -- Mean	SD	n	-- FZR-C[3] -- Mean	SD	n
Bh	24.0	5.0	2	28.3	9.4	3
Bs	20.2	-	1	20.1	9.2	2
Ex/Bx	8.1	0.3	2	12.0	3.2	3
Bx/Ex	-	-	-	17.7	-	1
Bt	-	-	-	19.9	-	1
C	-	-	-	13.2	-	1

Champion (coarse-loamy, mixed, frigid Typic Fragiorthods)

Soil[1] Hor.	-- FZR-A[2] -- Mean	SD	n	-- FZR-C[3] -- Mean	SD	n
Bh	22.9	3.6	7	38.0	15.7	7
Bs1	27.1	5.3	7	26.0	9.2	7
Bs2	23.2	8.7	4	22.8	10.2	4
Bs3	18.4	9.1	2	14.9	11.9	2
2Ex	17.8	3.7	2	16.2	3.9	2
2Bx1	4.0	6.3	3	9.4	2.9	3
2Bx2	2.4	3.7	3	8.1	1.2	3
2Bx3	3.6	4.8	2	7.6	2.5	2
2C	6.6	-	1	6.8	-	1

1 Soil Horizon 2 Frigid Zone Regression A
3 Frigid Zone Regression C
† Mean, ‡ Standard Deviation in mg S kg^{-1}

MESIC ZONE SOIL SERIES

In mesic zone Udipsamments (Table 8.4), results from all regressions indicated similar patterns of sulfate adsorption, predicted adsorption being highest in upper B horizons and decreasing with depth. Mesic zone Alfic Udipsamments had slight increases in sulfate adsorption in Bt horizons, similar to those predicted for frigid zone Alfic Udipsamments (Table 8.2). In mesic zone Typic Udipsamments (Table 8.4), low % clay in BC and C horizons may have produced under-prediction of sulfate adsorption by mesic zone regressions C and D (Table 7.6). In contrast, mesic zone regression B, based on exchangeable Al, pH, organic carbon and sum of bases, predicted higher adsorption, similar to patterns predicted for BC and C horizons of frigid zone Typic Udipsamments (Table 8.1), where % clay is also low.

Predicted sulfate adsorption in mesic zone Hapludalfs (Table 8.5) was characterized by noticeable peaks of adsorption in Bt and B/E horizons. An overall comparison of mesic zone soils suggests that sulfate adsorption is lowest in Udipsamments, increases slightly in Psammentic Hapludalfs, and is highest in coarse-loamy Hapludalfs and Glossoboric Hapludalfs such as the Oshtemo, Tekenink, and Remus series. A similar progression of increased sulfate adsorption was predicted by equations based on exchangeable Al, organic carbon, sum of bases and pH, and equations based on pH and % clay.

Table 8.4

Predicted Sulfate Adsorption in Mesic Zone Udipsamments

Oakville (mixed, mesic Typic Udipsamments)

Soil[1] Hor.	MZR-B[2] Mean†	SD‡	n	MZR-C[3] Mean	SD	n	MZR-D[4] Mean	SD	n	SPR-C[5] Mean	SD	n
Bw1	3.3	3.0	3	3.4	1.3	3	2.4	1.1	3			
Bw2	4.1	3.9	3	2.5	1.2	3	2.2	1.2	3	N.A.[6]		
BC	2.9	2.6	3	0.9	1.0	3	0.8	1.1	3			
C	1.8	1.6	3	0.9	0.4	2	0.8	0.2	2			

Plainfield (mixed, mesic Typic Udipsamments)

Soil[1] Hor.	MZR-B[2] Mean	SD	n	MZR-C[3] Mean	SD	n	MZR-D[4] Mean	SD	n	SPR-C[5] Mean	SD	n
Bw1	5.9	1.3	4	3.5	1.5	4	3.4	1.2	4			
Bw2	5.4	1.8	3	4.1	1.1	3	3.2	1.2	3	N.A.[6]		
BC	4.7	1.8	3	2.4	1.7	4	2.4	1.5	3			
C	2.1	1.7	3	0.7	0.8	4	0.3	1.3	3			

Mixed, Mesic Alfic Udipsamments (Coloma, Chelsea)

Soil[1] Hor.	MZR-B[2] Mean	SD	n	MZR-C[3] Mean	SD	n	MZR-D[4] Mean	SD	n	SPR-C[5] Mean	SD	n
Bw1	2.5	1.2	4	3.0	1.4	4	2.4	1.6	4	3.0	1.7	4
Bw2	2.7	2.2	4	1.8	1.2	4	2.0	1.8	4	1.6	1.4	4
E'	4.0	2.8	2	1.3	1.8	3	1.2	2.5	2	1.1	1.9	3
E'2	1.9	1.8	3	1.5	1.4	3	1.2	2.1	2	1.4	1.6	3
Bt	4.5	3.7	3	3.8	3.0	3	4.4	3.9	3	4.1	3.5	3

1 Soil Horizon
2 Mesic Zone Regression B
3 Mesic Zone Regression C
4 Mesic Zone Regression D
5 Spinks Series Regression C
6 Not Applicable
† Mean, ‡ Standard Deviation in mg S kg^{-1}

Table 8.5

Predicted Sulfate Adsorption in Mesic Zone Hapludalfs

Spinks (sandy, mixed, mesic Psammentic Hapludalfs)

Soil[1] Hor.	MZR-B[2] Mean[†]	MZR-B[2] SD[‡]	n	MZR-C[3] Mean	MZR-C[3] SD	n	MZR-D[4] Mean	MZR-D[4] SD	n	SPR-C[5] Mean	SPR-C[5] SD	n
E1	4.4	0.6	2	3.2	1.9	4	4.5	0.6	2	3.3	2.2	4
E2	2.1	1.7	2	2.8	1.8	4	3.3	1.6	2	2.8	2.0	4
E'	-	-	-	1.0	0.9	4	-	-	-	0.8	0.9	4
Bt	4.2	4.5	2	6.1	1.5	4	6.0	4.0	2	6.8	1.8	4

Remus (fine-loamy, mixed, mesic Glossoboric Hapludalfs)

Soil[1] Hor.	MZR-B[2] Mean	MZR-B[2] SD	n	MZR-C[3] Mean	MZR-C[3] SD	n	MZR-D[4] Mean	MZR-D[4] SD	n	SPR-C[5] Mean	SPR-C[5] SD	n
Bw1	6.9	3.2	3	6.2	1.2	3	5.6	0.7	3			
Bw2	5.2	2.1	3	6.2	2.4	3	6.1	2.8	3			
E/Bx	7.1	4.9	3	6.7	4.1	3	8.5	6.1	3			
B/Ex	17.5	12.5	3	12.5	4.7	3	16.9	8.4	3	N.A.[6]		
Bt1	12.1	6.0	3	11.8	2.5	3	15.1	2.9	3			
Bt2	1.6	1.0	2	6.0	1.8	2	4.6	0.8	2			
C	4.3	2.0	2	3.8	0.9	3	6.0	2.2	2			

Coarse-Loamy, Mixed, Mesic Hapludalfs (Tekenink, Oshtemo)

Soil[1] Hor.	MZR-B[2] Mean	MZR-B[2] SD	n	MZR-C[3] Mean	MZR-C[3] SD	n	MZR-D[4] Mean	MZR-D[4] SD	n	SPR-C[5] Mean	SPR-C[5] SD	n
E	4.8	4.3	3	3.4	1.5	4	2.2	2.1	3			
E/B	4.2	3.6	3	4.6	1.8	4	3.9	2.3	3			
E/Bt1	5.7	2.6	3	4.6	2.4	4	5.7	3.8	3			
Bt2	11.7	4.9	3	8.6	1.0	4	11.8	2.6	3	N.A.[6]		
BC	8.1	2.5	3	5.6	3.1	4	7.7	3.9	3			
Bt3	11.2	-	1	6.0	1.8	2	9.4	-	1			
C	-	-	-	1.5	1.1	3	-	-	-			

1 Soil Horizon
2 Mesic Zone Regression B
3 Mesic Zone Regression C
4 Mesic Zone Regression D
5 Spinks Series Regression C
6 Not Applicable
† Mean, ‡ Standard Deviation in mg S kg^{-1}

Tentative comparisons between frigid zone and mesic zone soils suggest that mesic zone Udipsamments (Table 8.4) have lower abilities to adsorb sulfate than similar frigid zone soils (Tables 8.1, 8.2), related to differences in pH, base saturation, and Al and Fe concentrations. These sandy mesic zone soils also were predicted to have substantially lower sulfate adsorption abilities than frigid zone Spodosols, Alfisols or finer textured mesic zone Hapludalfs. This suggests that the Michigan forest soils most sensitive to acid deposition in terms of consequences of sulfate leaching are located in southern lower Michigan where sulfate deposition and acid loading is highest (NADP, 1985a; 1985b; 1986). Further research will be required to test this hypothesis as mesic zone Udipsamments were not sampled during the present study.

COMPARISON OF DATA BASES

A comparison of the data developed from laboratory analysis of the soils sampled for this study with the data selected from the existing SCS/MTU soil characterization data base was made to determine the need for additional data to improve prediction of sulfate adsorption in Michigan forest soils. For frigid zone soils (Table 8.6), ranges and distributions of data were similar for bulk density, pH-H_2O, and pH-$CaCl_2$. Noticeable differences in range and distribution were present for organic carbon, DC-Fe, DC-Al, exchangeable Al, and sum of bases. This is not surprising,

Table 8.6

Comparison of Data Bases for Frigid Zone Soils

Property	Min.[1]	Med.[2]	90 %[3]	Max.[4]	%Analyzed[5]	Source[6]
B.D.†	1.06	1.56	1.86	2.02	50.6	SCS/MTU
g cm^{-3}	1.19	1.57	1.66	2.01	100.0	MSU
% Organic	0.00	0.19	1.34	3.70	84.8	SCS/MTU
Carbon	0.01	0.11	0.59	1.76	100.0	MSU
DC-Fe	<500	4000	9000	24000	68.0	SCS/MTU
mg kg^{-1}	410	1800	3970	5930	100.0	MSU
DC-Al	<500	2000	5000	11000	42.5	SCS/MTU
mg kg^{-1}	110	590	1760	3670	100.0	MSU
Exch Al	0.0	27.0	161.9	611.6	98.8	SCS/MTU
mg kg^{-1}	0.0	11.6	52.6	110.3	100.0	MSU
pH-H_2O	3.5	5.4	6.4	8.6	99.7	SCS/MTU
$-Log(H^+)$	4.8	5.5	6.6	8.9	100.0	MSU
pH-$CaCl_2$	3.3	4.8	6.2	7.8	74.2	SCS/MTU
$-Log(H^+)$	4.2	4.7	5.8	8.0	100.0	MSU
Σ Bases	0.0	0.5	4.7	77.5	94.7	SCS/MTU
cmol(+) kg^{-1}	0.0	0.2	3.0	27.3	100.0	MSU

1 Minimum
2 Median
3 90th percentile
4 Maximum
5 % of total samples analyzed for soil property
SCS/MTU n = 322 MSU n = 118
6 Source of Data
SCS/MTU Soil Conservation Service/Michigan Technological University (SCS-USDA, 1980; MTU-FFC, 1982-1984)
MSU Michigan State University, Department of Forestry
† Bulk Density

as a wider range of soils was selected from SCS/MTU soil characterization data than were sampled in the present study. Differences in DC-Fe and especially DC-Al were partly due to restriction of analyses to upper B horizons in the SCS/MTU data, but may also reflect regional differences in soil properties since SCS/MTU data included soils sampled in the upper peninsula of Michigan. Discrepancies may also exist due to methods of selection of pedons for sampling, as soils were randomly sampled for the present study, but were subjectively selected for sampling for SCS/MTU soil characterization studies. Some discrepancies may exist because of methods of horizon delineation and sampling; average horizon thicknesses tended to be greater in upper B horizons of frigid zone soils sampled for the present study than those of the same series sampled for SCS/MTU soil characterization studies. Analytical differences between laboratories, if present, are expected to be minor.

A comparison of data bases for mesic zone soils (Table 8.7) revealed that range and distribution of bulk density and both pH measures were similar, while relatively minor differences existed for % clay, organic carbon, DC-Fe, DC-Al, exchangeable Al, and sum of bases. Differences are largely attributable to the wider range of soils selected from the SCS/MTU data base.

The extent of information and data contained in the published soil characterization data reports (SCS-USDA, 1980; MTU-FFC, 1982-1984) was extremely impressive and

Table 8.7

Comparison of Data Bases for Mesic Zone Soils

Property	Min.[1]	Med.[2]	90 %[3]	Max.[4]	%Analyzed[5]	Source[6]
B.D.[†]	1.23	1.58	1.73	1.83	55.6	SCS/MTU
g cm^{-3}	1.29	1.56	1.65	1.86	100.0	MSU
Clay	0.0	3.6	13.7	25.8	100.0	SCS/MTU
%	1.4	6.0	11.6	16.1	100.0	MSU
% Organic	0.00	0.10	0.40	1.30	91.3	SCS/MTU
Carbon	0.01	0.08	0.23	0.45	100.0	MSU
DC-Fe	<500	3000	4000	6000	23.8	SCS/MTU
mg kg^{-1}	1430	4580	10330	12110	100.0	MSU
DC-Al	1000	1000	2000	2000	18.3	SCS/MTU
mg kg^{-1}	90	570	1040	1330	100.0	MSU
Exch Al	0.0	18.0	116.9	341.8	84.1	SCS/MTU
mg kg^{-1}	0.0	7.3	60.5	227.9	100.0	MSU
pH-H_2O	4.5	5.7	7.0	8.2	100.0	SCS/MTU
$-Log(H^+)$	4.6	5.8	8.4	9.0	100.0	MSU
pH-$CaCl_2$	3.9	4.9	6.5	7.6	94.4	SCS/MTU
$-Log(H^+)$	3.9	4.8	7.7	7.9	100.0	MSU
Σ Bases	0.0	0.7	5.6	32.2	98.4	SCS/MTU
cmol(+) kg^{-1}	0.1	1.3	11.2	19.3	100.0	MSU

1 Minimum
2 Median
3 90th percentile
4 Maximum
5 % of total samples analyzed for soil property
SCS/MTU n = 126 MSU n = 64
6 Source of Data
SCS/MTU Soil Conservation Service/Michigan Technological University (SCS-USDA, 1980; MTU-FFC, 1982-1984)
MSU Michigan State University, Department of Forestry
† Bulk Density

represents an immense effort in terms of physical labor, painstaking laboratory analysis, taxonomic correlation of sampled pedons, and editorial preparation for publication. The following ex post facto discussion of limitations of these data should in no way be taken as a negative criticism of that effort, but serves only as a caveat for those interested in using the data for the specific purpose of predicting sulfate adsorption in the soils described.

One limitation inherent in using existing soil characterization data to predict sulfate adsorption was the lack of complete analyses for certain properties in many pedons (Tables 8.6, 8.7, % Analyzed). This was especially apparent for DC-Fe and DC-Al, both variables important for prediction of sulfate adsorption. SCS/MTU soil characterization reports did not contain ammonium oxalate extraction data, a severe restriction since AO-Al was one of the soil properties most strongly associated with and predictive of sulfate adsorption ability in a variety of Michigan forest soils. Bulk density data was somewhat incomplete in SCS/MTU soil characterization data, a minor drawback since bulk density can be predicted using particle size analysis and organic matter content (Rawls, 1983), both variables well documented in SCS/MTU soil characterization data. Lack of complete DC-Fe, DC-Al, and bulk density data, however, prevented any meaningful application of linear discriminant functions to classify relative sulfate adsorption abilities of Michigan soils at this point. Other

limitations in using existing SCS/MTU data to predict sulfate adsorption were the few significant digits reported for DC-Fe and DC-Al concentrations, and reporting DC-Fe and DC-Al concentrations < 0.05% as trace (TR) amounts. These two variables were reported in increments of 0.1% (1000 mg kg^{-1}), producing an interval scale that could artificially affect regression estimates.

SCS/MTU exchangeable Al data were complete for most pedons, but their use to predict sulfate adsorption was limited by lack of sulfate adsorption data for soils high in exchangeable Al. The tendency for regression estimates based on exchangeable Al to predict higher sulfate adsorption than those based on DC-Al (Tables 8.2, 8.3) suggests that the relationship of adsorption to exchangeable Al or DC-Al departs from linearity for one or both at Al concentrations higher than those used to develop regression equations.

Comparison of data sets indicates that expansion of sulfate adsorption data to include soils higher in organic carbon, DC-Fe, DC-Al, exchangeable Al, and % clay is required for prediction of sulfate adsorption abilities over a wide range of soils. The need for sulfate adsorption data on additional soils, especially mesic zone Udipsamments, highly podzolized Haplorthods, and Fragiorthods, was also indicated. Expansion of the data base developed for this study to include additional soils and range of soil properties could be accomplished by incorporating selected

pedons from those sampled for the Ecological Classification System (ECS) project (Host, 1987) as well as by obtaining samples from pedons previously analyzed for SCS/MTU soil characterization studies, if available. Incorporation of SCS/MTU soil characterization samples would be attractive as only a few additional analyses (e.g. ammonium oxalate extractions) and sulfate adsorption determinations would be required. Inclusion of ECS samples would require more extensive soil analyses, but would allow estimates of sulfate adsorption abilities based on existing ecosystem classification units.

SUMMARY AND CONCLUSIONS

Existing Soil Conservation Service amd Michigan Technological University (SCS/MTU) soil characterizaton data and regression equations developed in the present study were used to predict sulfate adsorption in selected Michigan forest soils. Results suggested that mesic zone Typic Udipsamments had the lowest ability to retain sulfate. Other mesic and frigid zone Hapludalfs, frigid zone Udipsamments, and frigid zone Haplorthods were predicted to have moderate abilities to adsorb sulfate. Highest sulfate adsorption was predicted for Fragiorthods, based on extrapolated regression estimates for soils not sampled in the present study.

Comparison of the selected subset of the SCS/MTU soil characterization data base with the data obtained from the

present study indicated differences in range and distribution of data between data sets. These differences were attributed largely to the wider range of soils selected from SCS/MTU soil characterization data, along with differences in selection of soils for sampling. Limitations in use of existing soil characterization data to predict sulfate adsorption included lack of ammonium oxalate extraction data, incomplete data for bulk density and dithionite-citrate extractable Fe and Al, and reporting of few significant digits for Fe and Al data. Expansion of sulfate adsorption data and development of regression equations to include soils higher in organic carbon, dithionite-citrate extractable Fe and Al, exchangeable Al, and % clay would be required to predict sulfate adsorption in the entire range of Michigan forest soils thought to be sensitive to acid deposition.

Chapter IX

SUMMARY AND CONCLUSIONS

This chapter briefly summarizes research results and presents major conclusions, derived largely from sections at the ends of preceding chapters. Those interested in a more detailed discussion of specific methods or results are invited to examine the appropriate chapters in the body of the dissertation. A brief treatment of future research needs and directions is included at the end of this chapter.

The occurrence of acidic atmospheric deposition of anthropogenic origin raised concerns over potential effects on forest soils in Michigan. A preliminary classification indicated that over 70 soil series covering an estimated 40 percent of the land area of Michigan were potentially susceptible to adverse effects from acid deposition. Possible adverse effects include accelerated leaching of basic cations leading to loss of soil fertility over time. A major factor affecting soil sensitivity to cation loss resulting from acid deposition is the ability of the soil to adsorb or retain atmospherically deposited sulfate, as leaching losses of sulfate are accompanied by charge equivalents of cations. A problem in predicting effects of acid deposition on Michigan forest soils was that little was known concerning the relative abilities of these soils to adsorb sulfate.

The first objective of this study was to determine the ability of representative Michigan forest soils to adsorb sulfate under laboratory conditions and to determine initial levels of extractable sulfate present. The second objective was to relate sulfate adsorption to other soil properties commonly measured and used for soil classification. The final objective was to develop methods to predict sulfate adsorption which could be used to further classify the sensitivity of Michigan forest soils to effects of acid deposition related to sulfate leaching. The study was conducted in two stages, a preliminary study to determine appropriate sample preparation techniques and to test methodology, and a primary study designed to address the stated objectives.

Results of the preliminary study demonstrated that sulfate adsorption by soils under laboratory conditions was influenced by method of sample preparation. Air-dry samples from soil horizons with weak adsorptive capacities released more sulfate during adsorption equilibrations than did field-moist samples from the same horizons. Soil horizons with stronger sulfate adsorption characteristics adsorbed more sulfate after air-drying than if samples were kept field-moist. Differences in sulfate adsorption between air-dry and field-moist samples were least and correlations between soil preparations highest at solution concentrations of 25 mg S L^{-1} or less. It was concluded that laboratory studies using air-dry samples to examine relative sulfate

adsorption abilities of various soils should be performed at SO_4-S concentrations below 25 mg S L^{-1} to reduce discrepancies caused by air-drying.

A subset of Michigan soil series representing several gradients in soil physical and chemical properties affecting sulfate retention was selected for detailed study of sulfate adsorption. The series selected were considered to be potentially susceptible to adverse effects from acid deposition due to low cation exchange capacity, and were representative of soil taxonomic groups important as forest soils in the lower peninsula of Michigan. Series selected for study were Grayling (Typic Udipsamments), Rubicon (Entic Haplorthods), Kalkaska (Typic Haplorthods), Montcalm (Eutric Glossoboralfs), Spinks (Psammentic Hapludalfs), and Oshtemo (Typic Hapludalfs).

Six randomly located pedons of each series were sampled to allow statistical comparisons between series. Sampling locations were restricted to public lands with forest stands 40 years old or older that had soil profiles within the range of characteristics for the target series. Samples were obtained from soil pits; each mineral soil horizon down to and including the uppermost C horizon was sampled. Soil samples were air-dried and sieved prior to analysis. A relative measure of sulfate adsorption was determined by shaking air-dry samples in 0.01 M $CaCl_2$ solutions containing 10 mg S L^{-1}. Samples were shaken for 24 hours and then filtered. Solution filtrates were analyzed for SO_4-S and

sulfate adsorption was calculated from the disappearance of sulfate from solution. All soil samples were also analyzed for extractable SO_4-S; extractable P; dithionite-citrate, ammonium oxalate, and sodium pyrophosphate extractable Fe and Al; KCl exchangeable Al; ammonium acetate exchangeable Ca, Mg, K, and Na; organic carbon; and soil pH measured in both water and 0.01 M $CaCl_2$. Particle size analysis was performed on samples from the subsurface horizons of southern lower Michigan Spinks and Oshtemo pedons. Standard soil analysis methods were followed in all procedures.

All soil series studied had several horizons capable of adsorbing sulfate under laboratory conditions. Bw, Bs, and Bh horizons in frigid zone soils and E and Bt horizons in mesic zone soils displayed the highest abilities to adsorb sulfate. Total quantities of sulfate adsorbed and small reductions in solution sulfate concentrations during adsorption studies suggested that the soils investigated were relatively weak sulfate adsorbers, similar to forest soils in the northeastern United States.

No significant differences were found between series in total amounts of sulfate adsorbed under laboratory conditions when compared on the basis of adsorbed sulfate contents calculated to a depth of 150 cm in sulfate adsorbing horizons. Significant differences between series in sulfate adsorbing ability were present when comparing the upper 50 cm or the 100-150 cm depths in sulfate adsorbing horizons. In general, frigid zone series (Grayling,

Rubicon, Kalkaska, Montcalm) had major portions of their adsorption capacities concentrated in the upper 50 cm of the B horizon. In contrast, sulfate adsorbing capacity in mesic zone series (Spinks, Oshtemo) tended to be distributed more evenly throughout the solum. Frigid zone soils with limited adsorptive capacity in coarse-textured horizons in the lower solum (Grayling, Rubicon, Kalkaska) were thought to be more susceptible to rapid losses of cations associated with sulfate leaching from these depths in the soil profile. These results suggested that series differences in location of adsorption within the soil profile and flow path of percolating solutions may be more important in determining relative sensitivity to acid deposition than absolute differences in total adsorptive capacity.

Differences in extractable sulfate contents among frigid zone series suggested that more pronounced differences in amount or mode of sulfate retention exists under field conditions. Specifically, lower extractable sulfate contents in the Montcalm and Kalkaska series than in the Rubicon series suggested that either sulfate adsorption was higher in the Rubicon series, or the mode of sulfate retention differed in the Montcalm and Kalkaska Series, with microbially mediated incorporation of SO_4-S into organic forms predominating. High but variable levels of sulfate in the Spinks and Oshtemo series were related to variable levels of sulfate adsorption, higher but more variable sulfate deposition in southern lower Michigan, or to a

combination of these factors.

The consistent ability of all six series to adsorb sulfate from low concentration (10 mg S L^{-1}) sulfate solutions and positive correlations between adsorption and initial levels of extractable sulfate suggest that these series and similar Michigan forest soils are capable of retaining additional quantities of atmospherically deposited sulfate. Based on the range of calculated adsorption capacities of individual pedons (0.5 to 21.1 g S m^{-2} to 150 cm), individual soil bodies would have an ability to adsorb sulfate for periods from less than one to greater than 26 years at present average levels of deposition (0.8 g S m^{-2} yr^{-1}). This calculation assumes all sulfate deposited would be irreversibly adsorbed, but evidence based on known soil solution and groundwater sulfate concentrations under northern lower Michigan forests indicated that total retention of sulfate does not occur. Relative reversibility of adsorption was not investigated, but even temporary retention of sulfate via adsorption in the soil profile would buffer leaching effects resulting from impingement of acid deposition for periods measured in years or decades.

Significant correlations were present between sulfate adsorption and a variety of soil properties. Sulfate adsorption was consistently and positively correlated with extractable Fe and Al concentrations in a variety of soils. Strongest positive correlations existed with dithionite-citrate extractable Al and ammonium oxalate extractable Al

in subsurface horizons of both mesic and frigid zone series. Sulfate adsorption was negatively related to pH and base saturation in all soils studied. Positive correlations with extractable sulfate in subsurface horizons of all soils suggested that laboratory sulfate adsorption and past sulfate retention under field conditions were related. In frigid zone soils, positive correlation of sulfate adsorption with organic carbon in subsurface horizons was related to high correlation between organic carbon and Al and Fe fractions, or may have been related to sulfate retention through microbial S transformations in subsurface soil horizons high in organic carbon.

Results of regression analyses indicated that sulfate adsorption in typical Michigan forest soils could be predicted using relatively few variables derived from commonly measured soil properties. Maximum multiple regression R^2 values ranged from 0.85 to 0.94, depending on grouping of soils and specific predictors employed. The strongest, most consistent predictors were ammonium oxalate extractable Al, dithionite-citrate extractable Al, and exchangeable Al. Additional consistently significant predictors were dithionite-citrate extractable Fe, ammonium oxalate extractable Fe, and both pH-H_2O and pH-$CaCl_2$. Other variables that contributed to prediction in certain cases included % clay, organic carbon, extractable P, and extractable SO_4-S. Linear discriminant functions based on Al, Fe, organic carbon, and H^+ contents hold promise for

predicting relative sulfate adsorption ability on a pedon basis. Expansion of the data base to include more pedons with medium and high sulfate adsorption capacities would allow development of discriminant functions with improved classification accuracy.

Existing Soil Conservation Service and Michigan Technological University (SCS/MTU) soil characterization data and regression equations developed in the present study were used to tentatively predict sulfate adsorption in selected groups of Michigan forest soils. Results indicated that coarse-textured mesic zone Typic Udipsamments had the lowest predicted ability to adsorb sulfate, and would thus be most susceptible to adverse nutrient leaching effects from acid deposition. These soils occur in southern lower Michigan where sulfate deposition is highest. Other mesic and frigid zone Alfisols, frigid zone Udipsamments, and frigid zone Haplorthods were predicted to have similar moderate abilities to adsorb sulfate, as found in the present study. Highest sulfate adsorption was predicted for upper peninsula Fragiorthods, an extrapolation based on regression estimates for soils not sampled in the present study.

Comparison of SCS/MTU soil characterization data with the data gathered during the present study indicated differences in range and distribution of certain soil properties between data sets. These differences were largely attributable to the wider range of soils selected

from the SCS/MTU soil characterization data base. Discrepancies may also exist because of differences in methods of selecting sites for sampling. A random selection process was used in the current study while SCS/MTU soil characterization studies employed subjective selection. Limitations in use of existing soil characterization data to predict sulfate adsorption included lack of ammonium oxalate extraction data, incomplete data for bulk density and dithionite-citrate extractable Fe and Al, and reporting of few significant digits for Fe and Al data. Expansion of sulfate adsorption data and development of regression equations to include soils higher in organic carbon, dithionite-citrate extractable Fe and Al, exchangeable Al, and % clay would be required to predict relative sulfate adsorption abilities over the entire range of Michigan forest soils thought to be sensitive to acid deposition.

The present study provides a firm base for further study of sulfate adsorption processes in relation to acid deposition effects on Michigan forest soils and the forest ecosystems they support. Relative magnitudes of sulfate adsorption, soil horizons important in sulfate adsorption and retention, and soil properties related to sulfate adsorption have been established for a regional group of soils sampled with replication within a soil taxonomic framework. In addition, predictability of sulfate adsorption in the forest soils sampled using commonly measured soil properties was demonstrated.

Future research needs and directions include: 1) expanding data and predictive relationships to include soils with more extreme ranges in soil properties and sulfate adsorption abilities, 2) investigating southern lower Michigan Typic Udipsamments and associated forest ecosystems hypothesized to be especially vulnerable to acid deposition effects because of high rates of atmospheric sulfate deposition combined with low predicted sulfate adsorption ability, 3) refining sensitivity classification of Michigan forest soils in terms of sulfate adsorption capacities using soil taxonomic or ecosystem approaches, 4) researching the role of microbial S transformations and organic S fractions in sulfate retention in surface and subsurface forest soil horizons, and 5) performing field investigations on the influence of different soil profile morphologies on sulfate retention and cation leaching patterns dependent on soil moisture regimes and flow paths of soil water solutions.

APPENDIX A

APPENDIX A

MICHIGAN SOIL SERIES SENSITIVE TO ACID DEPOSITION

The following table listing Michigan soil series potentially sensitive to acid deposition was developed following criteria developed by McFee (1980). This classification is based largely on the cation exchange capacity and presence or absence of carbonates in the top 25 cm of soil, and presence or absence of flooding. If an acid input of 100 cm of pH 3.7 rain per year equals 10-25% of the cation exchange capacity in the top 25 cm, soils are rated as slightly sensitive. If this input exceeds 25% of the cation exchange capacity, the soils are considered sensitive. Soils with carbonates present in the upper 25 cm, soils experiencing frequent alluvial deposition, and soils with cation exchange capacities greater than 15.4 cmol (+) kg^{-1} are considered non-sensitive. While these criteria are limited, they did allow tentative estimates of soil sensitivity on a series level for Michigan soils. Information and data used to classify sensitivity of specific series was obtained from soil characterization studies conducted by the Soil Conservation Service (SCS-USDA, 1980; MTU-FFC, 1982-1984), supplemented by ratings contained in McFee (1980). This preliminary classification indicates that over seventy series covering an estimated forty percent of the land area of Michigan are potentially susceptible to adverse effects from acid precipitation.

Table A.1

Michigan Soil Series Potentially Sensitive to Adverse Effects from Acid Deposition: Preliminary Classification

Order / Series	Text[1]	Region[2]	%Extent[3]	pH[4]	CEC[5]	Rtg[6]
ALFISOLS						
Coarse-Loamy, Mixed, Frigid, Typic Eutroboralfs						
Emmet	SL	UP,nLP	.60	6.1-6.5	10-24	ss-ns
Omena	SL	nLP	mod.	6.1-7.8		
Coarse-Loamy, Mixed, Frigid, Eutric Glossoboralfs						
Hodenpyl	SL	nLP	sm.	4.5-5.5		
Montcalm	LS	nLP	.82	5.1-6.5	9.7	SS
Pemene	LfS	UP	mod.	4.5-5.5		
Hapludalfs						
Loamy, Mixed, Mesic, Arenic						
Okee	LfS	swLP	mod.	5.0-6.6	3.2-7.5	s-ss
Coarse-Loamy, Mixed, Mesic, Glossoboric						
Tekenink	LfS	cLP	mod.	4.7-7.3	5.2-6.9	s-ss
Fine-Loamy, Mixed, Mesic, Glossoboric						
Remus	SL	cLP	mod.	4.9-7.0	5.5-7.3	s-ss
Fine, Mixed, Mesic, Glossoboric						
Perrinton	L	sLP	mod.	4.6-7.0	10-17	ss-ns
Sandy, Mixed, Mesic, Psammentic						
Spinks	LS	sLP	.51	5.1-7.3	6-14	s-ss
Coarse-Loamy, Mixed, Mesic, Psammentic						
Arkport	LfS	sLP	mod.	4.5-7.3		

Table A.1 (continued)

Order / Series	Text[1]	Region[2]	%Extent[3]	pH[4]	CEC[5]	Rtg[6]
ALFISOLS						
Hapludalfs						
Coarse-Loamy, Mixed, Mesic, Typic						
Boyer	LS	sLP	.75	5.6-7.3		
Dryden	SL	sLP	.30	5.6-7.3		
Elmdale	SL	sLP	.10	5.1-7.3		
Hillsdale	SL	sLP	.75	5.1-7.3	5.1-7.1	s-NS
Lapeer	SL	LP	.75	5.6-6.5		
Oshtemo	SL	sLP	1.45	5.1-6.5	6.3	SS
Perrin	LS	sLP	mod.	5.6-7.3		
Fine-Loamy over Sandy/Sandy Skeletal, Mixed, Mesic, Typic						
Fox	Sil	sLP	1.39	5.6-6.5	14.2	SS
Ionia	SL	sLP	.60	4.5-6.5		
ENTISOLS						
Udipsamments						
Mixed, Frigid, Alfic						
Graycalm	S	eUP,nLP	.70	4.1-5.0	5.4-11	s-ss
Mixed, Frigid, Spodic						
Deer Park	fS	sUP,nwLP	.60	5.1-6.5		SS
Eastport	S	eUP,nLP	.60	5.6-7.8	4.9	s-SS
Mixed, Frigid, Typic						
Grayling	S	UP,nLP	1.49	4.5-5.8	2.8-12.4	s-SS
Omega	LS	UP	1.00	4.5-5.5	3.6-9.7	s-SS
Mixed, Mesic, Alfic						
Coloma	LS	sLP	.70	5.1-6.0	12.2	SS
Chelsea	LfS	sLP	mod.	5.1-7.3		
Mixed, Mesic, Typic						
Abscota	LS	sLP	.08	6.1-6.5		
Oakville	S	sLP	.78	4.7-7.3	8.1	ss
Plainfield	LS	sLP	1.99	4.4-7.3	4.4-10.4	S-ss

Table A.1 (continued)

Order	Series	Text[1]	Region[2]	%Extent[3]	pH[4]	CEC[5]	Rtg[6]
ENTISOLS							
Quartzipsamments							
Frigid, Uncoated, Typic							
	Shelldrake	S	UP	.10	4.5-6.0		SS
Udorthents							
Sandy-Skeletal, Mixed, Mesic							
	Mecosta	S	scLP	sm.	5.0-7.0	1.3-2.8	s
MOLLISOLS							
Sandy-Skeletal, Mixed, Udorthentic Haploborolls							
	Alpena	grSL	eUP,nLP	.20	6.6-7.8		SS
SPODOSOLS							
Fragiorthods							
Sandy, Mixed, Frigid, Alfic							
	Yalmer	S	nUP	mod.	4.6-6.0	9.9	ss
Coarse-Loamy, Mixed, Frigid, Alfic							
	Baraga	SiL	wUP	sm.	3.6-6.0	21.4	SS-ns
	Gogebic	fSL	wUP	1.60	4.5-6.0		
	Iron River	SiL	wcUP	.50	4.5-6.0	28.3	ns
	Kallio	SiL	wUP	sm.	4.5-5.5	30.8	ns
	McBride	SL	LP	.86	4.5-6.0	9.8	ss
	Munising	SL	nUP	1.60	4.5-6.0	9.6	SS
	Steuben	fSL	ncUP	mod.	4.5-6.0		
	Wakefield	SiL	wUP	.07	5.1-6.5		
Coarse-Loamy, Mixed, Frigid, Typic							
	Champion	SiL	wcUP	.50	3.6-6.0	29.4	SS-ns

Table A.1 (continued)

Order / Series	Text[1]	Region[2]	%Extent[3]	pH[4]	CEC[5]	Rtg[6]
SPODOSOLS						
Haplorthods, Alfic						
Sandy, Mixed, Frigid						
Blue Lake	LS	UP,nLP	.75	5.1-6.5		SS
Keeweenaw	LS	UP	.44	4.5-6.5	2.3-29	s-ns
Leelanau	LS	UP,nLP	.75	5.6-7.3		
Mancelona	LS	nLP	1.02	5.6-7.3	10.4	ss
Melita	S	eUP,nLP	.10	5.1-7.3		
Sandy over Loamy, Mixed, Frigid						
Menominee	LS	UP,nLP	.18	4.6-6.5	7.3	SS
Sandy over Clayey, Mixed, Frigid						
Manistee	LS	UP,nLP	.10	5.1-7.3		
Coarse-Loamy, Mixed, Frigid						
Alcona	SL	UP,nLP	.01	5.1-7.3	11-16	ss-ns
Trenary	fSL	UP	.90	5.1-6.5		SS
Ubly	SL	nLP	.12	5.6-6.5		
Coarse-Silty over Sandy or Sandy-Skeletal, Mixed, Frigid						
Stambaugh	SiL	wUP	.12	4.5-6.0		SS
Fine-Loamy, Mixed, Frigid						
Bohemian	SiL	UP,nLP	.13	5.1-6.5		SS
Isabella	L	nLP	.46	5.1-6.5		SS
Onaway	fSL	sUP,nLP	.46	5.1-7.3	9.4-23	ss-NS
Fine-Loamy over Sandy or Sandy Skeletal, Mixed, Frigid						
Newaygo	SL	ncLP	.60	5.6-6.5		
Haplorthods, Entic						
Sandy, Mixed, Frigid						
Croswell	S	UP,nLP	2.75	4.5-6.0	2.3-9.3	s-ss
Deerton	S	UP	sm.	3.6-6.0		
Duel	LS	seUP,nLP	.01	5.1-6.5		
East Lake	S	eUP,nLP	.70	5.6-7.3	9.7	ss
Ishpeming	S	wUP	sm.	4.5-6.0		

Table A.1 (continued)

Order	Series	Text[1]	Region[2]	%Extent[3]	pH[4]	CEC[5]	Rtg[6]
SPODOSOLS							
Haplorthods, Entic							
Sandy, Mixed, Frigid							
	Karlin	LfS	UP,nLP	.40	4.5-6.5		
	Kiva	SL	nLP	.40	6.1-7.8		
	Rousseau	fS	UP,nLP	.81	5.1-6.0	4.3-7.0	s-ss
	Rubicon	S	UP,nLP	2.25	4.5-6.0	2.7-10.4	s-SS
	Vilas	LS	UP	2.00	4.5-6.5		SS
Sandy, Mixed, Mesic							
	Covert	LS	sLP	.70	4.3-7.3	9.9	ss
	Grattan	S	sLP	large	4.5-6.5	7.7	ss
Coarse-Loamy, Mixed, Frigid							
	Longrie	L	UP,nLP	.34	5.6-7.3		SS
	Michigamme	fSL	wUP	.20	4.5-6.5	35.6	ns
Coarse-Loamy over Sandy or Sandy-Skeletal, Mixed, Frigid							
	Amasa	vfSL	wUP	.12	5.1-6.0	20.7	SS-ns
Haplorthods, Typic							
Sandy, Mixed, Frigid							
	Kalkaska	S	UP,nLP	2.75	4.4-6.0	1.1-16.4	s-ns
	Gilchrist	S	eUP,nLP	.10	5.1-7.8	12.1	SS
	Wallace	S	UP,nLP	.20	4.5-5.5		SS
Sandy-Skeletal, Mixed, Frigid							
	Waiska	SL	nUP	.05	4.5-6.0		
Coarse-Loamy, Mixed, Frigid							
	Chatham	fSL	eUP	sm.	6.1-7.8		SS
	Onota	SL	nwUP	.10	5.1-6.5		SS
Loamy-Skeletal over Sandy, Mixed, Frigid							
	Allouez	grSL	wUP	.16	4.5-6.0	17.3	SS-ns

Table A.1 (continued)

Order	Series	Text[1]	Region[2]	%Extent[3]	pH[4]	CEC[5]	Rtg[6]

1 Texture (from SCS-USDA; MTU-FFC, 1982-1984)

fS	fine sand	LS	loamy sand
fSL	fine sandy loam	S	sand
grSL	gravelly sandy loam	SiL	silt loam
L	loam	SL	sandy loam
LfS	loamy fine sand	vfSL	very fine sandy loam

2 Region of Occurrence (from SCS-USDA)

UP upper peninsula
LP lower peninsula
modifiers: n, northern; s, southern; e, eastern; w, western; c, central; and combinations of above.

3 % Extent: estimated % of total Michigan land area occupied by series (from Lumbert, 1981; SCS-USDA).
sm. < .1%, mod. .1 - .6%, large > .6 %.

4 pH, range, upper solum (from SCS-USDA; MTU-FFC, 1982-1984)

5 CEC, cmol (+) kg^{-1} (from McFee, 1980; SCS-USDA, 1980; MTU-FFC, 1982-1984). Average for upper 25 cm of solum.

6 Sensitivity Rating (from McFee, 1980)

S Sensitive, CEC < 6.2
SS Slightly Sensitive, CEC > 6.2 but < 15.4
NS Not Sensitive, CEC > 15.4, or carbonates present, or soil floods and receives alluvial deposition.
S, SS, NS - uppercase, directly from McFee, 1980.
s, ss, ns - lowercase, assigned based on other sources, but following McFee's rating scheme.

APPENDIX B

APPENDIX B

PEDON DESCRIPTIONS AND ANALYTICAL DATA FOR SAMPLED SOILS

This appendix contains soil profile descriptions and analytical data for the 38 pedons sampled for this study. Data for soil properties that can be calculated from the presented analytical data (e.g. sum of bases, effective CEC, % base saturation, crystalline Fe) have been omitted for brevity. Pedon descriptions are grouped alphabetically by series, order within series following that of assigned sampling blocks. Numbers in parentheses following soil horizon descriptions are laboratory sample numbers. Descriptions of soil property variables listed following pedon descriptions are given in Table B.1. See pages 61-62 for discussion of precision of analytical data.

Table B.1

Description of Soil Property Variables

Variable	Description - Soil Property	Units
SN†	Laboratory sample number	
HT	Average horizon thickness	cm
BD	Bulk density	g cm^{-3}
SADS	SO_4-S adsorbed from 10 mg S L^{-1}	mg S kg^{-1}
EXTS	Phosphate extractable SO_4-S	mg S kg^{-1}
DCFE	Dithionite-citrate extractable Fe	mg Fe kg^{-1}
DCAL	Dithionite-citrate extractable Al	mg Al kg^{-1}
AOFE	Ammonium oxalate extractable Fe	mg Fe kg^{-1}
AOAL	Ammonium oxalate extractable Al	mg Al kg^{-1}
NPFE	Sodium pyrophosphate extractable Fe	mg Fe kg^{-1}
NPAL	Sodium pyrophosphate extractable Al	mg Al kg^{-1}
PH2O	pH measured in 1:1 soil:H_2O	$-Log(H^+)$
PHCA	pH measured in 1:2 soil:0.01 M $CaCl_2$	$-Log(H^+)$
%ORGC	Organic carbon	%
EXTP	Bray #1 extractable P	mg P kg^{-1}
EXMG	Exchangeable Mg	mg Mg kg^{-1}
EXNA	Exchangeable Na	mg Na kg^{-1}
EXCA	Exchangeable Ca	mg Ca kg^{-1}
EXK	Exchangeable K	mg K kg^{-1}
EXAL	Exchangeable Al	mg Al kg^{-1}
CLAY	Clay, < 0.002 mm	%

† Laboratory sample number composed of descriptor codes:
First Digit = series code; 1 = Grayling, 2 = Kalkaska
3 = Montcalm, 4 = Oshtemo, 5 = Rubicon, 6 = Spinks
Second Digit = Block Number; Third Digit = Horizon Number

Series: Grayling Block: I Date Sampled: July 8, 1985
Location: Section 13, T31N R1E, Montmorency County, Michigan
2980' north and 1330' east of southwest section corner
Forest Cover: Mixed red and jack pine plantation
Stand Age (years): 44 Basal Area at Pit (ft^2 $acre^{-1}$): 100
Sampled By: Neil W. MacDonald

Pedon Description - Grayling Block I

A/E - 0 to 5 cm; N 2/0 sand; weak fine granular structure; very friable; many fine roots; abrupt smooth boundary (1110).

Bw1 - 5 to 22 cm; 7.5YR 4/4 sand; weak medium granular structure; very friable; many fine, medium, and large roots; 1-3% gravel; gradual smooth boundary (1120).

Bw2 - 22 to 42 cm; 7.5YR 4/6 sand; weak fine granular structure; very friable; common medium and few large roots; 3-5% gravel; clear smooth boundary (1130).

BC - 42 to 85 cm; 7.5YR 5/8 sand; weak medium subangular blocky structure; very friable; few medium and large roots; 5-7% gravel and cobbles; clear wavy boundary (1140).

C1 - 85 to 166 cm; 7.5YR 6/4 sand; single grain; loose; few medium and large roots; 3-5% gravel; few thin faint color bands present (1150).

C2 - 166 to 250 cm; auger sample indicated moderately effervescent coarse sand at 250 cm (not sampled).

Table B.2

Analytical Data - Grayling Block I

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
1110	4.8	1.198	-4.9	1.6	1674	821	733	942	754	966
1120	16.5	1.340	10.7	4.2	2643	1153	1213	1453	1136	1626
1130	20.0	1.481	12.4	6.5	2422	1116	764	1568	689	1421
1140	42.5	1.558	2.8	1.7	967	382	163	506	142	445
1150	81.2	1.565	.9	.2	709	163	117	209	98	225

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
1110	4.62	3.77	3.480	7.2	23.4	6.4	444.7	38.5	101.5
1120	5.05	4.38	.465	9.8	2.0	.9	33.2	8.3	50.5
1130	5.27	4.54	.258	11.4	.8	1.9	13.9	6.2	30.2
1140	5.53	4.87	.058	12.1	.3	4.1	6.0	2.5	5.6
1150	6.11	5.05	.042	5.6	1.2	.6	15.7	2.9	1.8

Series: Grayling Block: II Date Sampled: August 22, 1985
Location: Section 4, T24N R9W, Wexford County, Michigan
480' south and 1670' east of northwest section corner
Forest Cover: jack pine, black oak, and upland pin oak
Stand Age (years): 58 Basal Area at Pit (ft^2 $acre^{-1}$): 60
Sampled By: Neil W. MacDonald

Pedon Description - Grayling Block II

A/E - 0 to 7 cm; N 2/0 sand; weak fine granular structure; very friable; many fine and medium roots; small thin areas of E horizon present in spots; clear wavy boundary (1210).

Bw1 - 7 to 27 cm; 10YR 4/4 sand; weak coarse granular structure; very friable; common fine, medium, and few large roots; small thin areas of 7.5YR 3/4 associated with E horizon, <1% gravel; clear wavy boundary (1220).

Bw2 - 27 to 46 cm; 7.5YR 4/6 sand; weak coarse granular structure; very friable; common fine and medium roots; <1% gravel; clear smooth boundary (1230).

BC - 46 to 81 cm; 10YR 5/4 sand; weak coarse granular structure; very friable; few fine and medium roots; <1% gravel; sand becomes less coarse with depth; clear smooth boundary (1240).

C1 - 81 to 160 cm; 10YR 7/4 sand; single grain; loose; few medium roots; few faint organic or clay stains (1250).

C2 - 160 to 325 cm; auger sample indicated few faint 10YR 6/4 mottles below 165 cm; very slight effervescence at 230 cm; common faint 10YR 6/4 mottles at 310 cm; roots in mottled sand at 325 cm (not sampled).

Table B.3

Analytical Data - Grayling Block II

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
1210	6.7	1.115	-.9	2.4	1424	685	568	899	592	788
1220	19.5	1.379	11.9	14.2	2433	1670	1263	2530	892	1813
1230	19.3	1.468	8.4	18.6	1868	1133	601	1774	361	1204
1240	35.2	1.569	2.9	6.2	728	434	165	892	73	395
1250	79.3	1.582	1.1	1.7	602	196	104	368	37	266

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
1210	3.80	3.17	2.750	6.1	10.2	2.7	47.5	23.6	182.3
1220	4.84	4.38	.559	16.3	.8	1.7	3.2	6.7	52.2
1230	4.88	4.56	.278	15.2	.4	1.4	1.6	4.2	24.9
1240	5.00	4.76	.059	19.7	.1	1.1	1.0	2.4	6.5
1250	5.12	4.91	.032	18.4	.1	.5	.6	1.5	3.1

Series: Grayling Block: III Date Sampled: July 25, 1985
Location: Section 32, T25N R7E, Alcona County, Michigan
2100' north and 800' east of southwest section corner
Forest Cover: black oak and jack pine
Stand Age (years): 69 Basal Area at Pit (ft^2 $acre^{-1}$): 70
Sampled By: Neil W. MacDonald

Pedon Description - Grayling Block III

A/E - 0 to 6 cm; N 2/0 sand; weak medium granular structure; very friable; common fine and medium roots; clear smooth boundary (1310).

Bw1 - 6 to 21 cm; 7.5YR 4/4 sand; weak medium to coarse granular structure; very friable; common fine, medium, and large roots; 1-3% gravel; clear smooth boundary (1320).

Bw2 - 21 to 50 cm; 10YR 4/4 sand; weak medium granular structure; very friable; common fine roots; 7-10% gravel, largely in a stone line; clear smooth boundary (1330).

BC - 50 to 80 cm; 10YR 5/4 sand; weak medium granular structure; very friable; few fine and medium roots; 1% gravel; coarse sand in upper part of horizon underlying Bw2 gravel; gradual wavy boundary (1340).

C1 - 80 to 182 cm; 10YR 7/3 sand; single grain; loose; few medium roots; 1% gravel; few faint 10YR 5/4 stains; lenses of coarse sand; abrupt smooth boundary (1350).

C2 - 182 to 200 cm; 10YR 6/3 sand and gravel; single grain; loose; dark and light minerals intermixed; moderately effervescent (not sampled).

Table B.4

Analytical Data - Grayling Block III

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
1310	5.8	1.020	-7.6	3.7	2168	666	835	691	724	689
1320	14.8	1.407	12.3	5.5	3462	1424	968	1761	1054	1757
1330	28.5	1.513	9.3	8.7	2469	1052	435	1394	636	1451
1340	30.2	1.604	2.3	2.1	902	356	140	470	156	436
1350	101.7	1.599	-.3	.4	971	167	209	183	103	189

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
1310	4.88	4.19	3.391	8.8	34.3	3.5	641.9	53.5	33.6
1320	5.07	4.29	.536	8.2	3.2	2.1	25.0	10.8	66.2
1330	5.00	4.38	.212	17.3	1.5	2.2	9.0	7.2	36.5
1340	5.21	4.72	.057	17.8	.3	1.1	2.6	2.6	6.9
1350	6.65	5.79	.025	7.3	7.4	1.7	70.0	4.2	.1

Series: Grayling Block: IV Date Sampled: August 15, 1985
Location: Section 11, T26N R1E, Oscoda County, Michigan
1430' south and 250' east of northwest section corner
Forest Cover: jack pine and black oak, clump of older trees surrounded by jack and red pine 20 to 30 years old
Stand Age (years): 54 Basal Area at Pit (ft^2 $acre^{-1}$): 80
Sampled By: Neil W. MacDonald

Pedon Description - Grayling Block IV

A/E - 0 to 5 cm; N 2/0 sand; uncoated sand grains mixed throughout; weak medium granular structure; very friable; common fine and medium roots; abrupt smooth boundary (1410).

Bw1 - 5 to 20 cm; 7.5YR 3/4 sand; weak coarse granular structure; very friable; common medium and fine roots; 5% gravel; gradual smooth boundary (1420).

Bw2 - 20 to 41 cm; 7.5YR 4/6 sand; weak medium granular structure; very friable; common fine roots; 5-7% gravel and cobbles ending at clear smooth boundary (1430).

BC - 41 to 85 cm; 10YR 6/4 sand; single grain; loose; few fine roots in upper part; <1% gravel; clear smooth boundary (1440).

C1 - 85 to 160 cm; 10YR 6/3 sand; single grain; loose; gravel band from 127 to 137 cm with associated 7.5YR 4/6 color, common fine roots in gravel band (1450).

C2 - 160 to 255 cm; auger sample indicated layer of strongly effervescent sand between 190 and 200 cm; slightly effervescent coarse sand between 200 and 255 cm; strongly effervescent sand and gravel at 255 cm (not sampled).

Table B.5

Analytical Data - Grayling Block IV

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
1410	5.2	1.253	-3.0	2.4	2580	744	1013	658	927	1000
1420	15.3	1.443	9.6	6.2	3778	1509	1272	1594	964	1555
1430	20.8	1.576	7.6	4.4	2434	1031	633	1342	511	1088
1440	43.7	1.604	3.3	1.3	757	358	148	583	132	468
1450	75.0	1.605	1.6	.4	649	177	109	257	73	231

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
1410	4.77	3.93	3.157	5.0	20.2	1.9	217.1	52.3	74.0
1420	5.45	4.58	.510	15.3	7.0	.9	81.0	18.5	37.8
1430	5.62	4.69	.230	24.9	3.6	.8	43.4	8.9	20.3
1440	5.94	5.02	.054	16.9	.9	.5	10.5	3.4	3.5
1450	6.10	5.08	.025	8.9	1.0	.2	11.4	2.0	1.4

Series: Grayling Block: V Date Sampled: September 6, 1985
Location: Section 21, T20N R5W, Clare County, Michigan
1595' south and 1730' east of northwest section corner
Forest Cover: black oak and jack pine
Stand Age (years): 63 Basal Area at Pit (ft^2 $acre^{-1}$): 80
Sampled By: Neil W. MacDonald

Pedon Description - Grayling Block V

A/E - 0 to 5 cm; N 2/0 loamy sand; pale sand grains mixed throughout; weak fine granular structure; very friable; many fine and medium roots; clear smooth boundary (1510).

Bw1 - 5 to 26 cm; 7.5YR 4/4 sand with thin patches of 10YR 3/3 sand beneath A/E in spots; weak medium granular structure; very friable; common fine and medium roots; clear smooth boundary (1520).

Bw2 - 26 to 53 cm; 7.5YR 4/6 sand; weak coarse granular structure; very friable; many medium and large roots; 3-5% gravel and small cobbles; clear smooth boundary (1530).

BC - 53 to 102 cm; 10YR 5/6 sand; very weak coarse granular structure; very friable; few fine and medium roots; 2-3% gravel with stone line at clear smooth boundary (1540).

C1 - 102 to 165 cm; 10YR 6/4 sand; single grain; loose; common faint 10YR 5/4 blotches and stains (1550).

C2 - 165 to 330 cm; auger sample indicated sand became finer with depth; no gravel below 165 cm; very slight effervescence at 235 cm; few faint 10YR 6/6 mottles at 245 cm; no effervescence evident from 255 to 330 cm (not sampled).

Table B.6

Analytical Data - Grayling Block V

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
1510	5.3	1.033	-10.5	4.6	2838	962	1135	816	770	928
1520	20.7	1.511	13.3	3.8	3281	1000	1198	1257	987	1431
1530	27.2	1.609	11.6	5.4	2832	1008	790	1475	564	1197
1540	49.0	1.629	4.3	2.0	2008	558	410	744	286	668
1550	62.8	1.587	.7	.3	1134	133	253	207	110	167

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
1510	4.68	4.36	4.200	12.9	83.2	3.0	1014.4	56.6	18.5
1520	5.35	4.46	.329	18.4	8.9	1.1	61.4	8.3	43.8
1530	5.44	4.54	.125	36.6	3.7	1.3	21.9	6.3	25.8
1540	5.85	4.86	.070	23.8	2.5	1.1	14.9	3.9	7.8
1550	6.52	5.42	.015	7.5	4.7	.7	30.7	2.9	.5

Series: Grayling Block: VI Date Sampled: September 5, 1985
Location: Section 2, T17N R14W, Lake County, Michigan
300' north and 2960' east of southwest section corner
Forest Cover: black oak and jack pine
Stand Age (years): 61 Basal Area at Pit (ft^2 $acre^{-1}$): 100
Sampled By: Neil W. MacDonald

Pedon Description - Grayling Block VI

A/E - 0 to 7 cm; 10YR 2/1 sand; pale sand grains mixed throughout; weak fine granular structure; very friable; many fine and medium roots; clear smooth boundary (1610).

Bw1 - 7 to 22 cm; 7.5YR 3/4 sand; weak coarse granular structure; very friable; many fine, medium, and large roots; clear smooth boundary (1620).

Bw2 - 22 to 55 cm; 7.5YR 4/4 sand; weak coarse granular structure; very friable; many fine, medium, and large roots; <1% gravel; clear smooth boundary (1630).

BC - 55 to 98 cm; 10YR 5/4 sand; single grain; loose; few fine and medium roots; 1% fine gravel; clear wavy boundary (1640).

C - 98 to 165 cm; 10YR 6/4 sand; single grain; loose; few fine roots; 1% fine gravel (1650). Auger sample indicated no noticeable effervescence from 165 to 330 cm (not sampled).

Table B.7

Analytical Data - Grayling Block VI

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
1610	7.3	1.192	-4.3	2.5	2252	747	1233	1023	1067	1006
1620	14.7	1.472	12.9	5.4	2523	1533	1175	1879	1063	1954
1630	33.2	1.520	10.6	4.3	1963	1264	669	1609	455	1141
1640	42.8	1.658	2.8	1.7	743	416	156	703	141	444
1650	67.0	1.604	1.1	.8	483	171	74	255	82	239

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
1610	4.33	3.60	2.822	6.1	12.7	2.5	110.1	27.1	154.9
1620	5.22	4.55	.662	23.8	2.2	1.0	22.5	8.8	47.5
1630	5.59	4.73	.273	63.6	1.5	.7	16.7	4.5	18.9
1640	5.44	4.88	.051	38.7	.2	.4	2.7	1.5	4.3
1650	5.77	4.98	.024	14.8	.6	.7	3.4	1.9	2.6

Series: Grayling Block: VII Date Sampled: July 15, 1985
Location: Section 26, T27N R8W, Kalkaska County, Michigan
300' south and 300' west of northeast section corner
Forest Cover: jack pine
Stand Age (years): 46 Basal Area at Pit (ft^2 $acre^{-1}$): 100
Sampled By: Neil W. MacDonald and Doreen C. MacDonald

Pedon Description - Grayling Block VII

A/E - 0 to 3 cm; 10YR 2/1 sand; moderate medium granular structure; very friable; many fine and medium roots; abrupt smooth boundary (1710).

Bw1 - 3 to 18 cm; 10YR 3/3 sand; weak medium granular structure; very friable; many fine and medium roots; 1% gravel; clear wavy boundary (1720).

Bw2 - 18 to 49 cm; 7.5YR 4/6 sand; weak coarse granular structure; very friable; common fine and medium roots; 1% gravel; clear wavy boundary (1730).

BC - 49 to 130 cm; 10YR 5/6 sand; weak medium granular structure; very friable; common fine roots; 1-3% gravel; clear wavy boundary (1740).

C - 130 to 175 cm; 10YR 7/4 sand; single grain; loose; few medium and large roots; few faint 7.5YR 5/4 stains; 1-3% gravel (1750). Auger sample found no effervescence from 175 to 340 cm (not sampled).

Note: what apparently was a degraded E horizon was evident in parts of Bw1 horizon (not sampled); depth of solum was greater than typical for the Grayling series.

Table B.8

Analytical Data - Grayling Block VII

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
1710	3.3	1.202	-5.9	2.9	1877	441	727	413	584	515
1720	14.8	1.322	6.5	3.0	2616	1290	1083	1625	717	1341
1730	30.5	1.442	5.2	28.2	2215	985	693	1085	437	1046
1740	81.0	1.532	2.6	9.1	1173	455	263	818	202	698
1750	45.3	1.598	2.0	.4	665	112	135	136	80	163

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
1710	4.53	3.82	2.546	9.6	26.4	2.8	237.7	55.7	45.1
1720	6.07	5.17	.406	37.3	5.9	1.0	126.1	11.0	8.4
1730	5.17	4.66	.226	17.2	.9	1.5	9.2	4.1	17.4
1740	5.21	4.75	.083	16.6	.4	.4	4.2	2.4	6.5
1750	6.17	5.04	.026	4.5	3.2	1.9	15.7	3.6	1.3

Series: Kalkaska Block: I Date Sampled: July 11, 1985
Location: Section 23, T35N R1W, Cheboygan County, Michigan
2530' north and 100' east of southwest section corner
Forest Cover: red oak, red maple, mixed northern hardwoods
Stand Age (years): 65 Basal Area at Pit (ft^2 $acre^{-1}$): 110
Sampled By: Neil W. MacDonald

Pedon Description - Kalkaska Block I

A - 0 to 5 cm; N 2/0 loamy sand; moderate medium granular structure; very friable; many fine and medium roots; abrupt wavy boundary (2110).

E - 5 to 32 cm; 7.5YR 7/2 loamy sand; weak medium granular structure; very friable; many fine, medium, and common large roots; abrupt irregular boundary (2120).

Bh1 - 32 to 43 cm; 5YR 2.5/2 loamy sand; moderate medium subangular blocky structure; firm; 30% ortstein; few roots; clear irregular boundary (2130).

Bh2 - 43 to 86 cm; 7.5YR 3/4 sand; moderate medium subangular blocky structure; firm; 30% ortstein; few medium roots; gradual irregular boundary (2140).

Bs - 86 to 115 cm; 7.5YR 4/6 sand; weak medium subangular blocky structure; friable; 15% ortstein; few medium roots; clear irregular boundary (2150).

BC - 115 to 152 cm; 10YR 6/3 sand; weak medium granular structure; friable; few roots; clear wavy boundary (2160).

C - 152 to 167 cm; 10YR 6/3 sand; single grain; loose; few roots (2170). Auger sample indicated slightly effervescent sand at 305 cm (not sampled).

Table B.9

Analytical Data - Kalkaska Block I

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
2110	5.3	1.146	-3.5	2.4	1016	231	227	191	246	232
2120	26.7	1.511	.8	.1	547	56	22	79	22	56
2130	11.0	1.498	5.0	.7	2636	1511	1903	1903	1858	2146
2140	42.7	1.505	10.3	2.5	1965	1429	1230	2661	764	1533
2150	29.3	1.539	7.6	1.8	1600	901	738	1408	502	986
2160	37.0	1.606	2.1	.2	680	308	154	342	179	434
2170	15.0	1.564	.6	.1	520	203	103	355	124	351

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
2110	4.11	3.35	2.336	11.7	38.7	5.8	201.5	60.2	40.8
2120	4.40	3.70	.086	1.1	2.5	2.4	20.3	3.6	23.6
2130	5.80	4.80	.666	13.1	26.0	1.3	272.9	11.1	21.9
2140	5.62	4.66	.449	12.5	5.4	1.0	55.6	8.6	32.1
2150	5.66	4.68	.206	15.7	3.3	1.9	28.9	7.8	20.5
2160	5.95	4.83	.083	8.5	2.3	.8	24.4	4.8	6.5
2170	6.12	5.01	.036	6.8	2.0	2.1	29.2	4.3	4.2

Series: Kalkaska Block: II Date Sampled: July 17, 1985
Location: Section 20, T25N R9W, Grand Traverse County, MI.
250' south and 400' west of northeast section corner
Forest Cover: white pine, red oak, red maple, sugar maple
Stand Age (years): 65+ Basal Area at Pit (ft^2 $acre^{-1}$): 130
Sampled By: Neil W. MacDonald and Doreen C. MacDonald

Pedon Description - Kalkaska Block II

E - 0 to 10 cm; 10YR 4/2 loamy sand; weak medium granular structure; friable; many fine, medium, and large roots; clear wavy boundary (2210).

Bh - 10 to 29 cm; 7.5YR 3/4 loamy sand; weak coarse granular structure; very friable; 10% ortstein; many fine and medium roots; 5% gravel and cobbles; clear wavy boundary (2220).

Bs - 29 to 67 cm; 7.5YR 5/4 loamy sand; moderate medium subangular blocky structure; friable; 10% ortstein; common fine and medium roots; 5% gravel and cobbles; clear wavy boundary (2230).

BC - 67 to 137 cm; 10YR 4/4 loamy sand; weak coarse granular structure; very friable; few fine roots; 5% gravel; few thin 7.5YR 4/4 sandy loam lamellae; clear smooth boundary (2240).

C - 137 to 178 cm; 10YR 6/3 loamy sand; single grain; loose; few medium roots; thin 7.5YR 4/4 sandy loam lamellae at approximately 10 cm intervals (2250). Auger sample indicated no effervescence to 345 cm (not sampled).

Table B.10

Analytical Data - Kalkaska Block II

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
2210	10.3	1.358	.8	.6	1517	198	383	264	343	325
2220	19.2	1.194	14.2	2.3	4646	2420	3437	3885	2068	2215
2230	37.8	1.485	5.3	.8	2121	740	502	1046	453	1029
2240	69.5	1.608	2.5	.3	1406	275	267	390	318	555
2250	41.2	1.585	.9	.3	779	117	148	133	169	249

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
2210	4.75	3.80	.480	7.1	10.4	1.7	97.4	10.0	61.0
2220	5.75	4.84	.779	24.3	24.0	2.6	228.6	25.4	32.4
2230	6.12	5.02	.150	10.7	13.3	2.0	85.1	12.9	12.4
2240	6.11	4.93	.030	5.9	11.1	1.9	46.8	6.4	4.4
2250	6.44	5.27	.028	4.0	8.2	.9	37.7	4.2	.5

Series: Kalkaska Block: III Date Sampled: July 24, 1985
Location: Section 29, T31N R2E, Montmorency County, Michigan
3700' north and 3200' west of southeast section corner
Forest Cover: red maple, sugar maple, and black oak
Stand Age (years): 63 Basal Area at Pit (ft^2 $acre^{-1}$): 50
Sampled By: Neil W. MacDonald

Pedon Description - Kalkaska Block III

E - 0 to 25 cm; 10YR 6/2 loamy sand; weak medium granular structure; very friable; many fine, medium, and large roots; 1-3% gravel; clear irregular boundary (2310).

Bh - 25 to 48 cm; 5YR 3/3 to 7.5YR 3/4 loamy sand; moderate medium subangular blocky structure; firm; 20-30% ortstein; common fine and medium roots; clear irregular boundary (2320).

Bs - 48 to 76 cm; 7.5YR 4/6 loamy sand; moderate medium subangular blocky structure; very firm; 15-20% ortstein; common fine and medium roots; 1-3% gravel; gradual wavy boundary (2330).

BC - 76 to 154 cm; 10YR 5/4 loamy sand; weak coarse granular structure; very friable; few medium roots; clear smooth boundary (2340).

Bt - cumulative 7 cm thickness, faint to 6 cm thick 5YR 4/6 sandy loam lamellae present in BC horizon; weak medium subangular blocky structure; firm; clear smooth discontinuous boundary (2350).

C - 154 to 180 cm; 7.5YR 6/4 loamy sand; single grain; loose; few medium roots; few thin bands of Bt material that disappear with depth (2360). Auger sample indicated 7.5YR 6/4 calcareous loamy sand at 330 cm (not sampled).

Table B.11

Analytical Data - Kalkaska Block III

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
2310	24.7	1.485	.4	.4	761	67	124	104	60	77
2320	23.3	1.326	9.7	1.4	3271	1291	1970	1445	1910	1737
2330	27.7	1.532	6.4	1.6	1432	667	917	1117	715	859
2340	71.0	1.659	2.1	.4	746	286	285	577	271	499
2350	7.0	1.785	6.9	.3	2089	405	658	646	223	263
2360	26.3	1.657	1.3	.2	696	186	176	233	153	295

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
2310	4.31	3.54	.252	3.3	6.5	1.4	31.1	13.2	29.4
2320	5.43	4.41	.440	29.7	11.7	1.4	99.9	21.0	52.2
2330	5.50	4.50	.120	6.4	3.9	1.3	33.0	9.2	23.4
2340	5.79	4.61	.049	6.4	3.8	.7	28.7	7.2	12.3
2350	5.48	4.53	.078	7.0	60.9	3.4	277.1	46.9	26.6
2360	6.02	4.82	.031	6.4	9.5	1.5	53.7	10.6	5.3

Series: Kalkaska Block: IV Date Sampled: August 16, 1985
Location: Section 1, T27N R4W, Crawford County, Michigan
1500' south and 170' east of northwest section corner
Forest Cover: sugar maple, beech, and white birch
Stand Age (years): 70 Basal Area at Pit (ft^2 $acre^{-1}$): 110
Sampled By: Neil W. MacDonald

Pedon Description - Kalkaska Block IV

A - 0 to 4 cm; 10YR 2/1 loamy sand; weak fine granular structure; very friable; many fine and medium roots; clear wavy boundary (2410).

E - 4 to 18 cm; 10YR 5/2 loamy sand; weak fine granular structure; very friable; many fine, medium, and few large roots; 3% gravel; clear wavy boundary (2420).

Bh1 - 18 to 38 cm; 5YR 3/3 loamy sand; moderate medium subangular blocky structure; friable to firm; fragments of ortstein in lower part; many fine and medium roots; 3-5% gravel and cobbles; gradual irregular boundary (2430).

Bh2 - 38 to 53 cm; 7.5YR 3/2 sand; moderate medium subangular blocky structure; friable to firm; large chunks of ortstein in Bh2 tongues; common fine and medium roots; 3-5% gravel; clear irregular boundary (2440).

Bs - 53 to 95 cm; 7.5YR 4/4 sand; weak coarse granular structure; very friable; few fragments of ortstein; few fine and medium roots; 3-5% gravel; clear wavy boundary (2450).

BC - 95 to 153 cm; 10YR 4/4 sand; weak coarse granular structure; very friable; few fine and medium roots; 3% gravel; clear wavy boundary (2460).

C - 153 to 180 cm; 10YR 5/4 sand; single grain; loose; few medium roots; 1-3% fine gravel (2470). Auger sample indicated non-effervescent sand to 340 cm (not sampled).

Analytical Data - See Table B.12, page 189.

Series: Kalkaska Block: V Date Sampled: August 19, 1985
Location: Section 34, T24N R7W, Missaukee County, Michigan
2900' north and 1150' east of southwest section corner
Forest Cover: sugar maple and red maple
Stand Age (years): 61 Basal Area at Pit (ft^2 $acre^{-1}$): 100
Sampled By: Neil W. MacDonald

Pedon Description - Kalkaska Block V

A - 0 to 5 cm; 10YR 2/1 sand; weak fine granular structure; very friable; many fine and medium roots; some mixing with E apparent; clear wavy boundary (2510).

E - 5 to 26 cm; 5YR 5/2 to 7.5YR 5/2 sand; weak medium granular structure; very friable; many fine and medium roots; 1% gravel; abrupt irregular boundary (2520).

Bh1 - 26 to 37 cm; 5YR 3/2 sand; weak medium subangular blocky structure; friable; 15-20% ortstein occurring in tongues; 1-2% gravel; clear irregular boundary (2530).

Bh2 - 37 to 56 cm; 7.5YR 3/4 sand; weak coarse granular structure; very friable; some ortstein present; 1-2% gravel; clear irregular boundary (2540).

Bs - 56 to 76 cm; 7.5YR 4/4 sand; weak coarse granular structure; very friable; common fine and medium roots; 1-2% gravel; Bs present largely between Bh tongues; clear irregular boundary (2550).

BC - 76 to 129 cm; 10YR 5/4 sand; very weak medium granular structure; very friable; thin gravel bands in lower part; common fine and few medium roots in gravel bands; clear smooth boundary (2560).

C - 129 to 187 cm; 10YR 7/4 sand; single grain; loose; few fine and medium roots (2570). Auger sample indicated slightly effervescent sand at 275 cm; non-effervescent sand below to 345 cm (not sampled).

Analytical Data - See Table B.13, page 189.

Table B.12

Analytical Data - Kalkaska Block IV

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
2410	3.8	1.099	-8.7	4.3	1772	432	552	447	526	489
2420	14.2	1.439	.8	.4	1335	259	310	278	379	423
2430	20.3	1.383	11.3	1.2	4211	2081	1904	2468	2316	2432
2440	14.8	1.519	8.9	1.6	2524	1715	888	2443	1045	2072
2450	41.8	1.585	4.9	.6	1433	870	314	1198	493	1369
2460	58.3	1.595	2.6	.2	1196	427	237	575	373	921
2470	26.7	1.611	.6	.2	746	130	113	133	120	230

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
2410	5.22	4.60	2.657	11.6	55.5	1.7	656.5	50.1	4.9
2420	4.93	4.00	.530	3.2	7.9	1.1	112.4	7.7	39.1
2430	5.74	4.70	.786	13.6	12.1	1.8	221.9	12.8	35.5
2440	5.80	4.67	.414	12.8	5.5	1.5	108.8	11.9	36.2
2450	5.87	4.70	.248	8.9	4.4	.5	80.0	13.8	24.5
2460	5.78	4.66	.077	5.4	3.0	1.6	46.6	9.0	13.3
2470	6.12	4.95	.033	2.3	2.3	.7	31.8	3.9	2.1

Table B.13

Analytical Data - Kalkaska Block V

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
2510	4.8	1.215	-5.6	3.0	1319	183	271	157	240	105
2520	20.8	1.499	-.4	.7	966	155	225	205	211	179
2530	10.5	1.478	7.1	1.2	2598	1174	1447	1269	1708	1615
2540	19.2	1.474	9.1	1.3	2113	1908	1088	2201	1210	2192
2550	19.5	1.525	5.2	.5	1264	964	491	1101	518	1105
2560	52.7	1.637	2.5	.3	1034	441	205	659	153	516
2570	57.5	1.599	1.3	.2	556	273	134	514	88	322

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
2510	4.35	3.59	2.491	9.5	28.6	2.2	258.3	49.3	18.0
2520	4.39	3.72	.456	3.4	5.0	.8	38.4	10.8	33.5
2530	5.05	4.22	.577	13.4	4.6	1.3	49.2	8.9	64.9
2540	5.16	4.44	.528	18.7	2.4	1.3	23.6	6.2	42.7
2550	5.14	4.46	.280	18.3	1.2	1.1	12.0	4.0	25.6
2560	5.42	4.65	.089	12.1	.4	.3	6.1	2.6	11.0
2570	5.52	4.65	.070	7.4	.4	.7	5.8	3.2	8.7

Series: Kalkaska Block: VI Date Sampled: September 4, 1985
Location: Section 5, T20N R11W, Lake County, Michigan
880' south and 480' east of northwest section corner
Forest Cover: red pine plantation
Stand Age (years): 40 Basal Area at Pit (ft^2 $acre^{-1}$): 140
Sampled By: Neil W. MacDonald

Pedon Description - Kalkaska Block VI

A - 0 to 5 cm; N 2/0 loamy sand; weak fine granular structure; very friable; common fine and medium roots; some charcoal present at O/A interface; some disruption of A horizon due to furrowing for tree planting; clear wavy boundary (2610).

E - 5 to 17 cm; 10YR 5/2 sand; weak medium granular structure; very friable; common fine and medium roots; large dead roots present in some parts of E; clear irregular boundary (2620).

Bh - 17 to 40 cm; 5YR 2.5/2 to 7.5YR 3/4 sand; weak medium granular structure; friable; 5% ortstein occurring in chunks in lower Bh; clear wavy boundary (2630).

Bs - 40 to 59 cm; 7.5YR 4/6 sand; weak medium subangular blocky structure; friable; 5% ortstein; few medium roots; clear irregular boundary (2640).

BC - 59 to 91 cm; 10YR 5/4 sand; weak coarse subangular blocky structure; very friable; few medium roots; gradual irregular boundary (2650).

C - 91 to 165 cm; 10YR 6/4 sand; single grain; loose; few faint blotches, stains, and lines of darker color; few medium and large roots (2660). Auger sample indicated faintly effervescent sand from 255 to 325 cm (not sampled).

Table B.14

Analytical Data - Kalkaska Block VI

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
2610	4.8	1.275	-8.1	1.2	1623	474	561	511	528	465
2620	12.3	1.497	.3	.5	868	172	178	318	147	223
2630	22.5	1.329	20.0	17.8	4125	3674	2828	4883	1429	2674
2640	19.2	1.478	12.8	23.0	1955	1810	1066	3431	218	1053
2650	32.0	1.615	4.3	5.7	878	584	296	1090	107	468
2660	74.2	1.624	1.5	2.9	663	368	150	588	63	338

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
2610	4.25	3.80	2.460	11.6	24.6	1.3	287.9	51.5	69.2
2620	4.08	3.55	.460	2.2	2.7	.9	34.3	7.5	62.1
2630	4.98	4.40	.908	20.8	1.7	1.0	22.0	8.8	81.1
2640	5.08	4.66	.295	20.8	.6	.6	6.7	5.3	25.4
2650	5.07	4.68	.153	35.7	.3	.4	4.0	2.4	10.9
2660	5.14	4.78	.027	20.5	.1	.5	1.4	2.3	6.1

Series: Montcalm Block: I Date Sampled: July 23, 1985
Location: Section 35, T33N R1W, Cheboygan County, Michigan
1000' south and 200' east of northwest section corner
Forest Cover: sugar maple and beech
Stand Age (years): 70 Basal Area at Pit (ft^2 $acre^{-1}$): 80
Sampled By: Neil W. MacDonald

Pedon Description - Montcalm Block I

E - 0 to 12 cm; 10YR 4/2 loamy sand; weak medium granular structure; very friable; many fine, medium, and large roots; clear wavy boundary (3110).

Bh - 12 to 29 cm; 5YR 3/3 loamy sand; moderate coarse subangular blocky structure; friable to very firm; 10-25% cemented ortstein; common fine, medium, and few large roots; clear wavy boundary (3120).

Bs - 29 to 46 cm; 7.5YR 4/4 loamy sand; moderate medium subangular blocky structure; friable; 10-25% ortstein; few fine and medium roots; clear wavy boundary (3130).

E' - 46 to 59 cm; 7.5YR 5/4 loamy sand; moderate medium subangular blocky structure; firm; few fine roots; clear wavy discontinuous boundary (3140).

Bt - 59 to 75 cm; 5YR 4/4 sandy loam; weak medium subangular blocky structure; friable; few fine roots; clear wavy discontinuous boundary (3150).

E' & Bt - 75 to 145 cm; 7.5YR 6/4 loamy sand; single grain; loose (E'); few thin bands of Bt (3 cm total); few fine and medium roots; abrupt smooth boundary (3160).

C - 145 to 180 cm; 7.5YR 7/4 sand to loamy sand; single grain; loose; few fine and medium roots (3170). Auger sample indicated 10 cm thick Bt at 230 cm; calcareous sand from 240 to 280 cm; calcareous clay below 280 cm (not sampled).

Analytical Data - See Table B.15, page 192.

Table B.15

Analytical Data - Montcalm Block I

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
3110	12.3	1.475	-2.6	.8	1139	109	177	115	205	107
3120	17.3	1.406	8.0	1.8	4430	2678	2890	2646	3249	3304
3130	16.8	1.569	5.7	1.0	2284	1885	960	2082	950	2044
3140	13.0	1.566	3.4	.5	1577	947	374	1302	406	1238
3150	19.2	1.621	5.6	1.0	3051	899	526	1380	377	686
3160	67.3	1.551	.5	.1	545	166	111	172	116	234
3170	34.0	1.573	.2	.3	585	130	103	159	94	207

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
3110	4.63	3.78	.721	3.9	19.8	1.5	208.4	15.4	14.5
3120	5.38	4.49	1.765	13.8	20.2	2.9	396.9	11.4	67.7
3130	5.46	4.47	.763	17.5	4.3	1.9	140.8	5.5	60.7
3140	5.60	4.59	.268	7.3	2.2	.6	72.3	5.0	29.5
3150	5.49	4.54	.178	5.1	13.8	3.0	235.0	15.7	46.4
3160	6.10	4.95	.044	3.4	2.4	1.5	35.2	2.7	3.6
3170	6.25	5.10	.050	3.9	1.5	.4	33.3	1.9	1.7

Series: Montcalm Block: II Date Sampled: July 16, 1985
Location: Section 20, T31N R5W, Antrim County, Michigan
2580' north and 2450' west of southeast section corner
Forest Cover: sugar maple, beech, and basswood
Stand Age (years): 70+ Basal Area at Pit (ft^2 $acre^{-1}$): 130
Sampled By: Neil W. MacDonald and Doreen C. MacDonald

Pedon Description - Montcalm Block II

A - 0 to 5 cm; 10YR 2/1 loamy sand; weak medium granular structure; friable; many fine and medium roots; clear smooth boundary (3210).

E - 5 to 25 cm; 10YR 4/2 loamy sand; weak coarse granular structure; friable; common fine, medium, and large roots; <1% gravel; abrupt wavy boundary (3220).

Bh - 25 to 44 cm; 5YR 3/2 loamy sand; moderate medium subangular blocky structure; firm; common fine, medium, and large roots; clear wavy boundary (3230).

Bs - 44 to 83 cm; 7.5YR 4/4 loamy sand; weak coarse subangular blocky structure; friable; few fine roots; clear smooth boundary (3240).

E' & Bt - 83 to 136 cm; 10YR 5/4 loamy sand (E') and 7.5YR 5/4 sandy loam (Bt); Bt in thin bands and pockets; weak medium subangular blocky structure; firm; few fine roots; clear smooth boundary (3250).

Bt - 136 to 157 cm; 7.5YR 5/4 sandy loam; massive; friable; few fine roots; clear smooth boundary (3260).

2C - 157 to 164 cm; 10YR 6/4 silty clay loam; massive; firm; strongly effervescent (3270).

Table B.16

Analytical Data - Montcalm Block II

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
3210	5.0	.976	-10.2	5.1	975	207	254	230	169	110
3220	19.7	1.388	1.1	.5	822	88	148	121	152	129
3230	18.5	1.304	15.9	1.5	3997	2921	3393	4353	3026	3256
3240	38.7	1.513	12.1	1.1	2007	2176	1049	3619	605	1933
3250	52.8	1.670	5.2	.3	1854	525	352	747	487	925
3260	21.0	1.699	3.9	.3	4180	573	1137	720	422	362
3270	6.8	1.485	1.4	1.8	4489	633	1034	941	73	94

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
3210	4.79	4.00	4.000	17.1	63.3	3.4	630.4	64.7	5.2
3220	4.69	3.79	.353	1.6	6.4	1.3	56.2	10.2	23.4
3230	5.17	4.24	1.207	4.1	11.8	2.6	90.4	18.6	110.3
3240	5.56	4.54	.529	8.8	4.0	1.8	44.2	7.7	43.0
3250	5.54	4.38	.094	4.8	11.9	2.3	83.2	10.0	54.6
3260	6.50	5.72	.061	2.9	137.0	5.1	496.5	31.4	.9
3270	8.21	7.73	.236	5.3	510.0	16.7	4568.8	102.7	.0

Series: Montcalm Block: III Date Sampled: July 22, 1985
Location: Section 26, T32N R2E, Montmorency County, Michigan
1570' north and 3020' west of southeast section corner
Forest Cover: black oak, red maple, and bigtooth aspen
Stand Age (years): 68 Basal Area at Pit (ft^2 $acre^{-1}$): 100
Sampled By: Neil W. MacDonald

Pedon Description - Montcalm Block III

E - 0 to 8 cm; 10YR 4/2 loamy sand; weak medium granular structure; very friable; many fine and medium roots; abrupt wavy boundary (3310).

Bw - 8 to 47 cm; 10YR 4/4 loamy sand; weak medium subangular blocky structure; friable; common fine and medium roots; 5-7% gravel and cobbles; clear irregular boundary (3320).

E' - 47 to 83 cm; 7.5YR 6/4 loamy sand; weak coarse subangular blocky structure; friable; 3-5% gravel and cobbles; few medium roots; abrupt irregular boundary (3330).

Bt - 83 to 118 cm; 5YR 4/4 sandy loam; weak medium subangular blocky structure; firm; few medium roots; 5-7% gravel and cobbles; clear wavy boundary (3340).

C - 118 to 168 cm; 5YR 6/3 loamy sand to sandy loam; weak coarse subangular blocky structure; friable; few fine roots; 5-7% gravel and cobbles; strongly effervescent (3350).

Table B.17

Analytical Data - Montcalm Block III

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
3310	7.7	1.172	-3.6	2.4	1180	261	460	327	487	324
3320	39.3	1.503	4.0	1.8	1734	630	634	554	752	964
3330	36.2	1.556	1.1	.6	1074	172	213	245	182	286
3340	35.3	1.569	3.8	2.2	3943	678	735	1052	255	445
3350	50.0	1.664	-.3	.5	938	201	157	209	81	167

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
3310	4.26	3.54	1.642	6.9	17.4	1.9	169.2	33.2	48.2
3320	5.10	4.28	.333	17.1	4.7	1.4	32.0	14.4	48.0
3330	6.45	5.29	.019	9.1	11.8	1.3	88.3	12.8	2.7
3340	6.80	6.26	.112	6.0	94.0	6.0	958.7	64.6	.0
3350	8.87	7.86	.060	3.0	79.3	3.7	3991.1	23.0	.0

Series: Montcalm Block: IV Date Sampled: August 13, 1985
Location: Section 21, T20N R2W, Gladwin County, Michigan
1650' north and 620' west of southeast section corner
Forest Cover: White birch, red oak, and red maple
Stand Age (years): 56 Basal Area at Pit (ft^2 $acre^{-1}$): 110
Sampled By: Neil W. MacDonald

Pedon Description - Montcalm Block IV

A/E - 0 to 7 cm; 10YR 2/1 loamy sand; moderate medium granular structure; very friable; many fine and medium roots; clear smooth boundary (3410).

Bw - 7 to 52 cm; 7.5YR 4/6 loamy sand; weak medium subangular blocky structure; friable; common fine, medium, and large roots; 3-5% gravel; line of fine gravel at gradual smooth boundary (3420).

E' - 52 to 92 cm; 10YR 5/4 loamy sand; weak medium subangular blocky structure; very friable; few fine and medium roots; <1% gravel; abrupt wavy boundary (3430).

E' & Bt - 92 to 190 cm; 10YR 6/3 sand (E'); single grain; loose; few medium roots; clear wavy boundary; and 5YR 4/4 loamy sand to sandy loam (Bt); cumulative thickness 18 cm in lamellae 2-3 cm thick; massive; firm; few fine and medium roots; clear irregular boundary with C (Bt = 3440, E' = 3450).

C - 190 to 215 cm; 10YR 6/3 sand to loamy sand; single grain; loose; few medium roots; strongly effervescent (3460).

Table B.18

Analytical Data - Montcalm Block IV

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
3410	7.2	1.036	-7.8	4.5	4020	713	1316	581	631	481
3420	44.7	1.610	6.0	1.2	4126	666	644	638	640	916
3430	40.0	1.602	1.3	.4	1717	232	251	137	297	335
3440	18.0	1.629	5.3	.7	5933	778	1085	655	623	489
3450	80.3	1.569	1.4	.2	1669	168	335	137	194	200
3460	24.8	1.562	.4	.2	1453	162	375	99	161	224

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
3410	5.56	4.90	2.881	27.8	132.4	2.5	910.9	96.8	2.1
3420	5.79	4.72	.162	24.7	9.9	1.5	88.1	8.5	16.5
3430	6.19	5.02	.020	4.5	4.2	1.0	65.7	4.0	1.6
3440	6.29	5.22	.104	4.1	56.1	3.1	427.2	26.0	2.8
3450	6.43	5.24	.042	2.7	6.5	1.1	86.2	4.5	.5
3460	8.86	7.78	.042	3.3	28.9	2.1	2059.1	5.9	.0

Series: Montcalm Block: V Date Sampled: August 21, 1985
Location: Section 1, T22N R11W, Wexford County, Michigan
610' south and 1120' east of northwest section corner
Forest Cover: sugar maple, hemlock, black cherry, white ash
Stand Age (years): 60+ Basal Area at Pit (ft^2 $acre^{-1}$): 120
Sampled By: Neil W. MacDonald

Pedon Description - Montcalm Block V

A/E - 0 to 13 cm; 10YR 2/1 loamy sand; weak medium granular structure; very friable; many fine and medium roots; small pockets of E horizon material present in places; clear wavy boundary (3510).

Bw1 - 13 to 28 cm; 10YR 3/3 loamy sand; weak coarse granular structure; friable; many fine and medium roots; 1-2% gravel; clear irregular boundary (3520).

Bw2 - 28 to 86 cm; 7.5YR 4/6 loamy sand; weak medium subangular blocky structure; friable; common fine and medium roots; 3-5% gravel; clear smooth boundary (3530).

E'x & Bt - 86 to 146 cm; 10YR 5/3 loamy sand (E'x); weak medium subangular blocky structure; firm (dense and brittle); few fine roots; and 5YR 5/4 sandy clay loam (Bt); massive; firm; total 33 cm in bands and pockets intermingled in E'; clear irregular boundary (E'= 3540, Bt = 3550).

C1 - 146 to 161 cm; 7.5YR 5/4 sandy loam; massive; friable; violently effervescent; abrupt smooth discontinuous boundary (3560).

2E'& Bt - 161 to 258 cm; 10YR 6/3 sand E'; and 7.5YR 5/6 loamy sand Bt; single grain; loose; pockets of calcareous sand; auger sample from 195 to 258 cm (3570).

2C2 - 258 to 333 cm; 7.5YR 5/4 loamy sand and gravel; moderately effervescent; auger sample (3580).

Analytical Data - See Table B.19, page 198.

Series: Montcalm Block: VI Date Sampled: September 3, 1985
Location: Section 8, T18N R8W, Osceola County, Michigan
180' south and 550' west of northeast section corner
Forest Cover: red oak, red maple, and bigtooth aspen
Stand Age (years): 78 Basal Area at Pit ($ft^2\ acre^{-1}$): 140
Sampled By: Neil W. MacDonald

Pedon Description - Montcalm Block VI

E - 0 to 6 cm; 10YR 5/2 loamy sand; weak fine granular structure; very friable; many fine and medium roots; 10-15% gravel and cobbles; clear smooth boundary (3610).

Bw1 - 6 to 33 cm; 7.5YR 3/4 loamy sand; weak coarse granular structure; very friable; many fine, medium, and large roots; 10-15% gravel and cobbles; gradual smooth boundary (3620).

Bw2 - 33 to 57 cm; 10YR 4/4 loamy sand; weak medium subangular blocky structure; friable; common fine, medium, and large roots; 5-7% gravel and cobbles; clear wavy boundary (3630).

E' - 57 to 88 cm; 10YR 5/3 sand to loamy sand; weak medium subangular blocky structure; friable; few fine and medium roots; 3-5% gravel and cobbles; clear irregular boundary (3640).

E' & Bt - 88 to 199 cm; 10YR 6/2 sand to loamy sand (E'); single grain; loose; few fine and medium roots; 2-3% gravel and cobbles; abrupt wavy boundary; and 5YR 4/4 sandy loam (Bt); massive; firm; cumulative thickness 49 cm in bands 0.5 to 10 cm thick; few fine and medium roots; abrupt wavy boundary (Bt = 3650, E' = 3660).

C - 199 to 216 cm; 7.5YR 5/4 loamy sand; weak medium subangular blocky structure; friable; 2-3% gravel and cobbles; violently effervescent (3670).

Analytical Data - See Table B.20, page 198.

Table B.19

Analytical Data - Montcalm Block V

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
3510	13.2	1.336	-3.4	2.9	2984	511	1193	617	742	474
3520	15.2	1.538	10.4	1.0	3787	1147	1653	1060	1984	1704
3530	58.2	1.604	8.4	1.5	3062	1072	760	1482	751	1288
3540	27.0	1.742	4.2	.2	2288	446	364	447	304	547
3550	33.2	1.839	-.5	.8	3211	462	567	527	285	373
3560	14.8	2.014	.4	1.1	2312	290	385	308	114	170
3570	96.5	1.624	-.2	.4	763	120	143	98	126	184
3580	75.0	1.659	.1	.3	1064	157	201	115	195	281

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
3510	4.86	4.32	1.309	6.1	41.1	1.6	377.3	35.3	20.3
3520	5.24	4.31	.611	5.0	10.7	1.3	119.2	17.1	65.5
3530	5.41	4.47	.218	14.0	1.9	.9	25.7	5.9	42.6
3540	5.87	4.57	.102	3.6	14.2	1.8	115.6	9.3	26.6
3550	8.10	7.45	.101	4.5	187.0	4.4	1064.7	25.4	.0
3560	8.65	7.86	.046	2.6	128.0	4.2	3565.6	23.5	.0
3570	8.72	7.70	.011	2.2	26.3	1.0	485.6	4.4	.0
3580	8.85	7.91	.027	2.1	36.0	2.4	1394.7	7.0	.0

Table B.20

Analytical Data - Montcalm Block VI

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
3610	5.8	1.378	-.9	1.5	1730	237	472	359	455	291
3620	26.7	1.231	18.6	19.6	5229	3016	3335	3538	2463	2917
3630	24.3	1.545	11.7	13.9	2687	1313	953	2075	505	1122
3640	30.7	1.669	4.2	3.2	1478	423	326	741	254	544
3650	48.7	1.729	4.9	1.2	4416	601	803	573	244	160
3660	62.0	1.666	1.1	.7	1297	185	257	191	184	260
3670	16.8	1.788	.8	.6	1888	207	348	195	195	282

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
3610	3.98	3.33	.933	14.7	13.1	2.4	39.8	28.6	108.0
3620	4.84	4.30	.796	50.5	2.7	.6	11.8	19.9	103.4
3630	5.12	4.56	.226	28.8	1.4	1.2	7.6	10.0	36.3
3640	5.82	4.78	.039	13.7	6.9	1.3	23.6	8.2	11.8
3650	6.48	5.50	.042	4.6	134.5	3.0	417.4	39.7	2.0
3660	6.34	5.09	.013	4.5	16.6	1.3	49.2	7.6	2.0
3670	8.81	7.98	.019	3.1	75.5	2.9	3606.1	17.4	.0

Series: Montcalm Block: VII Date Sampled: July 9, 1985
Location: Section 36, T33N R2E, Presque Isle County, MI.
4370' north and 1620' west of southeast section corner
Forest Cover: red oak, white oak, and bigtooth aspen
Stand Age (years): 48 Basal Area at Pit (ft^2 $acre^{-1}$): 80
Sampled By: Neil W. MacDonald

Pedon Description - Montcalm Block VII

A - 0 to 3 cm; N 2/0 loamy sand; moderate fine granular structure; very friable; common fine and medium roots; clear smooth boundary (3710).

E - 3 to 8 cm; 10YR 5/2 loamy sand; weak medium granular structure; very friable; common fine and medium roots; 5-7% gravel and cobbles; abrupt smooth boundary (3720).

Bs - 8 to 33 cm; 7.5YR 4/6 loamy sand; weak coarse granular structure; friable; common fine, medium and large roots; 5-10% gravel and cobbles; clear wavy boundary (3730).

E' - 33 to 51 cm; 7.5YR 5/4 loamy sand; weak medium subangular blocky structure; firm; common medium roots; 5-10% gravel and cobbles; abrupt wavy boundary (3740).

2Bt - 51 to 64 cm; 5YR 3/4 sandy clay loam; weak medium subangular blocky structure; very firm; few medium roots; 15-20% gravel and cobbles; abrupt irregular boundary (3750).

2C - 64 to 112 cm; 5YR 4/4 sandy clay loam; weak medium subangular blocky structure; firm; few fine roots; some root channels with Bt material; 15-20% gravel and cobbles; moderately effervescent (3760).

Note: The 2Bt and 2C horizons were too high in clay to fall within the Montcalm series range of characteristics.

Table B.21

Analytical Data - Montcalm Block VII

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
3710	2.7	1.036	-18.2	6.9	1260	310	480	381	396	300
3720	4.7	1.284	-.8	.4	989	137	309	169	292	202
3730	25.0	1.502	8.0	2.2	2964	1362	1940	1549	1740	1916
3740	17.5	1.634	5.1	1.1	1791	523	541	790	457	710
3750	12.5	1.893	3.1	1.2	5832	934	1071	1594	216	338
3760	47.7	1.788	.8	.3	2518	379	447	522	111	227

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
3710	4.85	4.16	4.381	25.1	88.6	3.3	787.7	124.2	5.7
3720	4.50	3.66	.542	8.5	9.8	2.3	42.7	18.7	34.7
3730	5.25	4.44	.516	73.7	11.1	.8	85.4	21.7	53.1
3740	5.50	4.49	.135	13.8	9.0	2.1	31.1	13.3	26.0
3750	7.78	7.05	.212	6.8	172.1	7.3	1561.9	71.8	.0
3760	8.52	7.69	.049	2.2	113.5	5.0	4161.6	40.6	.0

Series: Oshtemo Block: I Date Sampled: July 2, 1985
Location: Section 14, T3N R7E, Oakland County, Michigan
2280' north and 1055' east of southwest section corner
Forest Cover: white oak and black oak
Stand Age (years): 51 Basal Area at Pit (ft^2 $acre^{-1}$): 90
Sampled By: Neil W. MacDonald and Doreen C. MacDonald

Pedon Description - Oshtemo Block I

A - 0 to 10 cm; 10YR 3/2 loamy sand; moderate medium granular structure; friable; many fine and medium roots; 1% gravel; clear irregular boundary (4110).

E1 - 10 to 64 cm; 10YR 5/6 loamy sand; weak fine subangular blocky structure; friable; common medium and large roots; 3-5% gravel; clear wavy boundary (4120).

E2 - 64 to 80 cm; 7.5YR 5/6 sandy loam; weak medium subangular blocky structure; friable; few fine and medium roots; 3% gravel; clear wavy boundary (4130).

Bt1 - 80 to 94 cm; 7.5YR 4/6 sandy loam; moderate coarse subangular blocky structure; friable; common fine and medium roots; 3% gravel; gradual wavy boundary (4140).

Bt2 - 94 to 152 cm; 7.5YR 4/6 sandy loam; moderate medium subangular blocky structure; friable; common fine and medium roots; 10-15% gravel; abrupt irregular boundary (4150).

2C - 152 to 198 cm; 10YR 5/3 sand and gravel; single grain; loose; few fine roots; 10-15% gravel; moderately effervescent (4160).

Table B.22

Analytical Data - Oshtemo Block I

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
4110	9.8	1.065	-10.9	5.9	4392	763	1910	899	1079	593
4120	54.0	1.530	5.4	2.1	3923	511	757	427	379	515
4130	16.3	1.581	5.0	1.4	5251	523	749	387	343	422
4140	14.3	1.585	7.9	3.3	7813	738	1442	741	513	628
4150	57.7	1.452	6.4	2.9	7248	689	1452	535	182	159
4160	45.8	1.563	-.1	.4	2548	153	623	109	75	74

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL	CLAY
4110	5.57	5.01	3.051	19.8	120.2	4.7	879.6	77.8	3.2	-
4120	5.22	4.35	.163	15.3	21.1	2.6	62.0	9.2	34.5	5.5
4130	5.63	4.67	.054	12.8	63.5	3.5	157.4	12.8	11.5	5.5
4140	5.83	4.83	.062	16.2	108.4	5.2	323.9	21.4	9.0	7.6
4150	5.84	4.98	.129	10.7	98.3	6.5	438.7	19.1	6.5	9.6
4160	8.82	7.81	.027	2.6	48.6	3.4	2507.1	5.7	.0	2.5

Series: Oshtemo Block: II Date Sampled: July 30, 1985
Location: Section 35, T2N R1E, Ingham County, Michigan
2810' north and 1020' east of southwest section corner
Forest Cover: red pine plantation
Stand Age (years): 39 Basal Area at Pit (ft^2 $acre^{-1}$): 190
Sampled By: Neil W. MacDonald and Doreen C. MacDonald

Pedon Description - Oshtemo Block II

Ap - 0 to 20 cm; 10YR 3/3 sandy loam; moderate coarse granular structure; friable; common fine and medium roots; 3-5% gravel; abrupt smooth boundary (4210).

E - 20 to 55 cm; 10YR 4/4 sandy loam; moderate coarse subangular blocky structure; friable; few fine and common medium roots; 3-5% gravel; clear wavy boundary (4220).

Bt1 - 55 to 74 cm; 7.5YR 4/6 sandy loam; moderate medium subangular blocky structure; friable; few fine and medium roots; 3-5% gravel; abrupt smooth boundary (4230).

Bt2 - 74 to 105 cm; 7.5YR 4/4 sandy loam; moderate medium subangular blocky structure; firm; few fine and medium roots; <1% gravel; clear wavy boundary (4240).

BC - 105 to 156 cm; 10YR 4/4 loamy sand; weak medium subangular blocky structure; friable; few fine and medium roots; <1% gravel with thin band of coarse sand and gravel at 155 cm; clear smooth boundary (4250).

2C - 156 to 211 cm; 10YR 5/3 sand; single grain; loose; few fine roots; with few fine bands of 7.5YR 4/6 sandy loam; massive; firm (4260). Auger sample indicated non-effervescent coarse sand from 211 to 265 cm; effervescent coarse sand at 265 cm (not sampled).

Table B.23

Analytical Data - Oshtemo Block II

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
4210	20.0	1.499	3.2	6.6	5044	818	1633	918	710	1004
4220	34.7	1.528	7.6	6.6	5413	579	911	760	409	604
4230	18.5	1.533	6.1	5.6	8180	673	1041	501	367	441
4240	31.0	1.599	5.0	6.2	7463	643	1213	459	507	647
4250	51.2	1.549	-.4	1.8	4977	333	1226	267	253	306
4260	54.7	1.492	.7	.8	3772	223	715	130	132	165

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL	CLAY
4210	4.68	3.95	.512	8.8	6.6	2.7	49.7	15.0	89.7	-
4220	5.29	4.32	.174	8.9	15.5	6.9	74.5	7.2	37.7	7.8
4230	5.86	4.92	.071	3.0	27.1	5.5	348.9	14.7	6.3	7.7
4240	5.93	5.05	.075	3.6	34.4	9.5	344.0	16.0	3.3	6.7
4250	6.88	6.15	.065	6.3	31.8	3.3	177.4	7.1	.0	2.9
4260	7.23	6.16	.032	4.5	21.1	2.5	104.7	4.1	.0	1.8

Series: Oshtemo Block: III Date Sampled: August 3, 1985
Location: Section 8, T1N R4E, Livingston County, Michigan
3196' north and 1834' west of southeast section corner
Forest Cover: red oak, white oak, and shagbark hickory
Stand Age (years): 70 Basal Area at Pit (ft^2 $acre^{-1}$): 120
Sampled By: Neil W. MacDonald

Pedon Description - Oshtemo Block III

A - 0 to 9 cm; 10YR 2/2 loamy sand; weak coarse granular structure; very friable; common fine and medium roots; 1% gravel; clear smooth boundary (4310).

E - 9 to 66 cm; 10YR 4/4 loamy sand; weak medium subangular blocky structure; friable; common fine, medium, and large roots; 15-20% gravel, cobbles, and boulders; gradual smooth boundary (4320).

Bt1 - 66 to 95 cm; 7.5YR 4/6 gravelly sandy loam; moderate medium subangular blocky structure; firm; common fine roots; 10-15% gravel; clear wavy boundary (4330).

Bt2 - 95 to 116 cm; 5YR 4/6 gravelly sandy loam; moderate coarse subangular blocky structure; firm; few fine and medium roots; 10-15% fine gravel; clear wavy boundary (4340).

BC - 116 to 139 cm; 10YR 4/4 loamy sand; single grain; loose; few fine roots; discontinuous irregular boundary (4350).

2C - 139 to 187 cm; 10YR 5/3 sand and gravel; single grain; loose; few medium roots; strongly effervescent (4360).

Table B.24

Analytical Data - Oshtemo Block III

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
4310	9.0	1.303	-5.1	4.7	4837	898	2189	1068	1161	841
4320	57.2	1.499	2.5	1.1	4201	490	1033	441	472	397
4330	28.5	1.545	9.7	2.9	8326	944	1139	599	268	222
4340	20.8	1.603	2.0	5.5	9312	1104	1294	811	148	165
4350	23.3	1.510	1.8	1.6	3726	383	728	312	228	277
4360	48.2	1.541	.0	.1	2413	160	428	112	95	118

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL	CLAY
4310	4.84	4.11	1.594	31.9	44.2	2.6	270.0	34.2	58.4	-
4320	5.81	4.78	.126	15.5	47.3	2.0	130.7	11.3	9.8	4.7
4330	5.38	4.52	.098	11.5	88.5	5.6	366.4	24.4	20.4	9.0
4340	6.35	5.84	.115	5.7	134.8	7.9	753.1	35.8	1.1	10.0
4350	6.56	5.65	.062	4.2	32.9	2.8	212.7	8.8	.2	3.0
4360	8.96	7.78	.049	1.2	50.2	3.1	3020.1	5.8	.1	1.7

Series: Oshtemo Block: IV Date Sampled: August 7, 1985
Location: Section 16, T1S R3E, Washtenaw County, Michigan
2030' north and 1950' west of southeast section corner
Forest Cover: bur oak, black oak, and red oak
Stand Age (years): 91 Basal Area at Pit (ft^2 $acre^{-1}$): 110
Sampled By: Neil W. MacDonald and Doreen C. MacDonald

Pedon Description - Oshtemo Block IV

Ap - 0 to 16 cm; 10YR 2/2 sandy loam; moderate coarse granular structure; friable; many fine, medium, and large roots; abrupt smooth boundary (4410).

E - 16 to 60 cm; 10YR 4/3 sandy loam; moderate medium subangular blocky structure; friable; common fine, medium, and large roots; 5-7% gravel and cobbles; clear irregular boundary (4420).

Bt1 - 60 to 93 cm; 7.5YR 4/6 sandy loam; moderate coarse subangular blocky structure; very firm; few medium roots; 5-7% gravel; gradual smooth boundary (4430).

Bt2 - 93 to 128 cm; 7.5YR 4/6 sandy loam; moderate medium subangular blocky structure; firm; few medium roots; 3-5% gravel; clear smooth boundary (4440).

BC1 - 128 to 155 cm; 10YR 4/4 sandy loam; weak medium subangular blocky structure; friable; few medium roots; 3-5% gravel (4450).

Composite bucket auger samples taken 1-19-86: BC2 - 155 to 165 cm; 10YR 4/4 sandy loam (4460). BC3 - 165 to 190 cm; 10YR 4/4 sandy loam (4470). C - 190 to 218 cm; 10YR 5/4 sandy loam (4480). BC2, BC3, and C samples were taken adjacent to the pit site; cobbles and boulders below 225 cm prevented investigation of deeper material.

Analytical Data - See Table B.25, page 205.

Series: Oshtemo Block: V Date Sampled: August 26, 1985
Location: Section 27, T1S R9W, Kalamazoo County, Michigan
1230' north and 1390' west of southeast section corner
Forest Cover: red oak, black oak, and white oak
Stand Age (years): 71 Basal Area at Pit (ft^2 $acre^{-1}$): 90
Sampled By: Neil W. MacDonald

Pedon Description - Oshtemo Block V

Ap - 0 to 13 cm; 10YR 2/1 sandy loam; weak medium granular structure; friable; many fine and medium roots; 1-3% gravel; clear smooth boundary (4510).

E1 - 13 to 45 cm; 10YR 4/4 loamy sand; weak fine subangular blocky structure; friable; common fine, medium, and large roots; 3-5% gravel and cobbles; gradual smooth boundary (4520).

E2 - 45 to 77 cm; 7.5YR 5/4 loamy sand; moderate medium subangular blocky structure; friable; few fine and medium roots; 7-10% gravel and cobbles; clear wavy boundary (4530).

Bt1 - 77 to 91 cm; 7.5YR 4/4 gravelly sandy loam; moderate medium subangular blocky structure; firm; common fine and medium roots; 7-10% gravel; clear wavy boundary (4540).

Bt2 & BC - 91 to 130 cm; 7.5YR 4/6 sandy loam (Bt2); weak medium subangular blocky structure; friable; common fine and medium roots; 3-5% gravel and cobbles; clear irregular boundary (4550); and 7.5YR 5/6 loamy sand (BC); 10 cm total occurring as pockets and bands; single grain; loose; few fine and medium roots (4560).

2C - 130 to 166 cm; 10YR 6/4 sand and gravel; single grain; loose; few medium roots; strongly effervescent (4570).

Analytical Data - See Table B.26, page 205.

Table B.25

Analytical Data - Oshtemo Block IV

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
4410	16.0	1.135	-7.8	8.5	5270	1324	2316	1496	1472	1189
4420	44.0	1.557	3.8	2.6	5142	619	1351	644	738	631
4430	33.3	1.859	12.4	21.5	12114	1333	2107	877	368	323
4440	34.5	1.611	7.9	19.0	10328	999	1650	661	310	244
4450	27.2	1.564	3.2	4.4	5799	490	845	270	439	406
4460	10.0	1.564	3.4	10.4	7899	767	1202	413	348	255
4470	25.0	1.612	3.8	13.2	10595	951	1517	647	466	249
4480	27.5	1.530	-1.0	8.9	9000	817	1586	612	458	285

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL	CLAY
4410	5.20	4.66	2.622	24.2	104.0	3.4	751.8	66.4	15.6	-
4420	5.09	4.25	.328	24.0	17.5	2.1	84.0	15.7	44.7	7.8
4430	5.23	4.36	.089	4.4	122.5	3.7	359.0	48.4	31.3	16.1
4440	5.33	4.53	.089	5.2	84.7	3.8	284.9	31.9	15.9	10.8
4450	5.60	4.60	.080	8.9	35.9	2.1	146.5	11.4	6.5	5.3
4460	5.45	4.64	.106	8.6	65.3	6.1	272.4	22.2	9.7	8.6
4470	5.43	4.68	.104	8.2	88.8	4.6	384.1	24.0	11.9	10.8
4480	5.63	4.79	.108	6.8	92.5	5.1	404.8	17.6	6.7	11.6

Table B.26

Analytical Data - Oshtemo Block V

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
4510	12.5	1.198	-7.4	5.3	4839	1117	1923	1132	1147	1054
4520	31.7	1.535	1.2	1.3	4422	718	1282	1082	612	793
4530	32.2	1.542	-.3	.9	4142	449	630	312	402	510
4540	14.0	1.635	.0	2.1	10675	1040	2265	834	194	206
4550	28.7	1.611	.6	1.3	5961	609	1485	561	141	128
4560	10.0	1.590	.5	.2	3020	295	724	270	288	403
4570	36.0	1.590	-.5	.2	2330	145	450	78	159	137

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL	CLAY
4510	5.27	4.92	2.429	53.7	111.8	2.6	798.0	92.7	4.3	-
4520	5.67	4.67	.227	108.3	26.9	1.5	138.8	24.6	20.1	7.2
4530	5.99	5.06	.093	54.7	26.4	1.4	154.7	19.3	5.7	5.5
4540	7.02	6.56	.167	35.8	221.5	4.5	1012.3	57.7	.0	13.7
4550	6.43	5.77	.070	22.6	97.7	2.5	425.5	29.3	.0	6.5
4560	7.92	7.03	.035	17.7	64.0	1.4	465.4	14.3	.0	3.4
4570	8.83	7.74	.017	6.4	42.6	2.6	2175.2	4.6	.4	2.2

Series: Oshtemo Block: VI Date Sampled: August 28, 1985
Location: Section 6, T7S R12W, St. Joseph County, Michigan
2450' north and 440' west of southeast section corner
Forest Cover: red oak, white oak, and pignut hickory
Stand Age (years): 130 Basal Area at Pit ($ft^2\ acre^{-1}$): 120
Sampled By: Neil W. MacDonald

Pedon Description - Oshtemo Block VI

A - 0 to 11 cm; 10YR 3/1 sandy loam; weak medium granular structure; very friable; common fine and medium roots; 1% gravel; clear smooth boundary (4610).

E - 11 to 47 cm; 10YR 5/4 sandy loam; weak fine subangular blocky structure; friable; common fine, medium, and large roots; 2-3% gravel; clear wavy boundary (4620).

Bt1 - 47 to 70 cm; 7.5YR 4/4 sandy loam; moderate coarse subangular blocky structure; very firm; common fine and medium roots, 2-3% gravel; clear smooth boundary (4630).

Bt2 - 70 to 95 cm; 7.5YR 4/6 sandy loam; weak medium subangular blocky structure; friable; common fine and medium roots; common gravel bands; clear smooth boundary (4640).

Bt3 & BC - 95 to 187 cm; 7.5YR 4/6 sandy loam (Bt3); weak medium subangular blocky structure; friable; 41 cm total in bands and layers (4650); and 10YR 5/6 loamy sand (BC); single grain; loose; few fine and medium roots; thin layers of calcareous gravel; clear smooth boundary (4660).

2C - 187 to 325 cm; 10YR 6/4 sand; single grain; loose; auger sample (4670). Strongly effervescent, faintly mottled coarse sand below 325 cm (not sampled).

Table B.27

Analytical Data - Oshtemo Block VI

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
4610	11.3	1.236	-3.4	3.6	5107	1463	1808	1590	1023	1309
4620	36.0	1.504	6.1	3.7	4424	920	1312	1113	718	692
4630	23.3	1.612	15.2	9.0	5978	963	1311	905	297	482
4640	25.0	1.611	15.2	10.3	5532	784	1183	770	185	341
4650	40.7	1.648	9.5	7.9	5078	591	1218	573	113	200
4660	51.0	1.596	1.7	3.4	2872	282	516	213	265	433
4670	137.7	1.556	-.1	1.0	2089	186	498	121	187	268

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL	CLAY
4610	6.10	5.59	2.325	73.3	146.1	2.2	1257.7	136.6	1.1	-
4620	4.99	4.10	.292	94.1	14.7	1.7	73.2	27.5	111.0	10.6
4630	4.74	3.88	.088	18.8	53.0	2.0	106.0	41.5	227.9	11.6
4640	4.91	4.00	.066	14.4	72.9	1.9	125.1	44.8	154.2	9.6
4650	5.21	4.29	.031	14.5	83.3	2.2	199.2	51.9	33.2	6.9
4660	5.67	4.74	.021	9.2	35.1	1.3	105.8	17.6	3.4	2.6
4670	8.08	7.08	.005	8.0	32.4	1.3	180.2	7.4	.0	1.4

Series: Rubicon Block: I Date Sampled: July 10, 1985
Location: Section 21, T35N R1E, Cheboygan County, Michigan
300' south and 260' west of northeast section corner
Forest Cover: red pine, black oak, and jack pine
Stand Age (years): 44 Basal Area at Pit (ft^2 $acre^{-1}$): 60
Sampled By: Neil W. MacDonald

Pedon Description - Rubicon Block I

A - 0 to 4 cm; N 2/0 sand; weak medium granular structure; very friable; many fine roots; abrupt smooth boundary (5110).

E - 4 to 9 cm; 10YR 4/2 sand; weak medium granular structure; very friable; common fine and medium roots; abrupt smooth boundary (5120).

Bs1 - 9 to 27 cm; 7.5YR 3/4 sand; weak medium granular structure; very friable; common fine, medium, and large roots; <1% gravel; clear smooth boundary (5130).

Bs2 - 27 to 48 cm; 7.5YR 5/6 sand; weak coarse granular structure; very friable; common fine and medium roots; <1% gravel; clear smooth boundary (5140).

BC - 48 to 106 cm; 7.5YR 6/4 sand; weak medium granular structure; very friable; few fine roots; clear smooth boundary (5150).

C - 106 to 166 cm; 7.5YR 6/4 sand; single grain; loose; thin, faint color bands at 6-10 cm intervals (5160). Auger sample indicated similar non-effervescent sand to 330 cm (not sampled).

Table B.28

Analytical Data - Rubicon Block I

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
5110	3.5	1.193	-16.2	6.3	1161	374	385	336	428	412
5120	4.8	1.376	-.6	.8	823	173	284	209	288	294
5130	17.7	1.399	9.5	5.0	2534	1569	954	1717	747	1453
5140	21.2	1.579	4.6	3.9	920	421	235	1106	170	633
5150	58.0	1.590	2.3	1.5	449	221	104	514	57	280
5160	59.8	1.551	1.6	.6	408	160	78	283	44	208

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
5110	4.40	3.89	3.137	15.9	28.5	5.6	338.9	37.2	28.4
5120	4.54	3.72	.564	2.9	6.3	1.1	66.0	9.2	50.4
5130	5.06	4.39	.475	9.9	2.1	1.8	17.9	11.7	47.9
5140	5.16	4.66	.025	12.4	.5	.4	4.0	2.9	10.9
5150	5.43	4.90	.017	17.5	.3	.9	2.1	2.6	3.4
5160	5.93	5.07	.028	16.2	.5	.5	3.5	2.3	2.8

Series: Rubicon Block: II Date Sampled: July 12, 1985
Location: Section 4, T29N R2W, Otsego County, Michigan
3430' north and 290' west of southeast section corner
Forest Cover: black oak, red maple, and bigtooth aspen
Stand Age (years): 63 Basal Area at Pit (ft^2 $acre^{-1}$): 30
Sampled By: Neil W. MacDonald

Pedon Description - Rubicon Block II

A - 0 to 3 cm; 10YR 2/1 loamy sand; weak medium granular structure; very friable; many fine roots; abrupt smooth boundary (5210).

E - 3 to 9 cm; 10YR 6/2 sand; weak medium granular structure; very friable; common fine and medium roots; clear wavy boundary (5220).

Bs1 - 9 to 39 cm; 7.5YR 4/6 sand; weak coarse subangular blocky structure; friable; 5-10% ortstein; common fine, medium, and large roots; 1-3% gravel; gradual smooth boundary (5230).

Bs2 - 39 to 62 cm; 7.5YR 5/6 sand; weak coarse granular structure; very friable; common fine, medium and large roots; 1-3% gravel; clear wavy boundary (5240).

BC - 62 to 131 cm; 10YR 6/6 sand; single grain; loose; few fine roots; 5-10% gravel; 10YR 5/4 color band at clear wavy boundary (5250).

C - 131 to 187 cm; 10YR 6/4 sand; single grain; loose; few medium and large roots (5260). Auger sample indicated thin 7.5YR 4/6 loamy sand bands at 10-15 cm intervals from 187 to 305 cm; non-calcareous gravelly sand at 305 cm (not sampled).

Table B.29

Analytical Data - Rubicon Block II

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
5210	2.8	1.098	-4.0	2.8	1225	272	339	282	338	220
5220	5.5	1.434	1.7	1.2	1446	385	488	351	566	493
5230	29.7	1.369	15.6	8.4	2889	1692	1332	2365	925	1740
5240	22.5	1.424	11.9	9.8	1882	1049	639	1936	411	1129
5250	68.7	1.600	3.0	1.8	1418	367	209	494	206	510
5260	55.8	1.576	1.7	.2	837	143	124	148	157	280

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
5210	4.10	3.36	2.499	11.3	42.0	4.3	239.0	73.4	55.3
5220	4.54	3.72	.926	6.4	9.0	2.2	56.6	15.1	78.6
5230	5.20	4.46	.482	16.8	3.2	1.4	17.4	7.5	48.5
5240	5.11	4.54	.218	19.8	1.0	1.9	4.5	5.1	29.6
5250	5.56	4.72	.020	11.0	1.0	1.0	7.7	2.6	7.5
5260	6.36	5.09	.014	4.3	4.7	1.2	29.9	3.7	1.3

Series: Rubicon Block: III Date Sampled: July 26, 1985
Location: Section 15, T26N R2E, Oscoda County, Michigan
3430' north and 2600' west of southeast section corner
Forest Cover: red maple, black oak, bigtooth aspen, red pine
Stand Age (years): 65 Basal Area at Pit (ft^2 $acre^{-1}$): 90
Sampled By: Neil W. MacDonald

Pedon Description - Rubicon Block III

A - 0 to 4 cm; N 2/0 loamy sand; moderate medium granular structure; very friable; many fine and medium roots; abrupt smooth boundary (5310).

E - 4 to 14 cm; 7.5YR 6/2 sand; weak medium granular structure; very friable; common fine, medium, and large roots; clear smooth boundary (5320).

Bs1 - 14 to 34 cm; 7.5YR 4/6 sand; weak medium granular structure; very friable; common medium and large roots; clear smooth boundary (5330).

Bs2 - 34 to 52 cm; 10YR 4/6 sand; weak medium subangular blocky structure; friable; 5% ortstein in lower part; few medium roots; clear smooth boundary (5340).

BC - 52 to 107 cm; 10YR 6/4 sand; moderate coarse subangular blocky structure; friable; 15-20% ortstein in strongly cemented, massive, chunks at 55-70 cm; few medium roots; gradual wavy boundary (5350).

C - 107 to 175 cm; 10YR 7/4 sand; single grain; loose; few medium roots (5360). Auger sample indicated few, fine, distinct 10YR 6/8 mottles or stains between 160 and 335 cm; C horizon non-calcareous to 335 cm (not sampled).

Table B.30

Analytical Data - Rubicon Block III

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
5310	4.2	1.197	-12.8	6.6	805	216	343	389	297	217
5320	10.3	1.423	-1.5	1.2	554	82	59	77	89	113
5330	20.2	1.444	18.4	9.9	3442	2089	2322	3817	908	1445
5340	17.8	1.488	12.4	13.1	1760	1205	929	2983	331	981
5350	54.8	1.633	2.6	6.4	746	474	312	1039	174	522
5360	67.7	1.588	1.8	.1	783	257	176	508	76	260

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
5310	4.33	3.51	2.398	8.4	32.7	2.9	269.8	82.6	37.2
5320	4.26	3.55	.315	2.2	4.8	1.8	36.7	12.5	29.5
5330	5.25	4.49	.502	8.4	3.1	.7	33.2	13.7	45.1
5340	5.49	4.79	.219	12.2	1.9	1.2	19.7	5.0	11.5
5350	5.27	4.73	.084	18.7	.8	.6	7.9	2.7	6.8
5360	5.97	4.94	.033	10.9	1.2	.9	10.0	3.7	3.9

Series: Rubicon Block: IV Date Sampled: August 14, 1985
Location: Section 28, T24N R2E, Ogemaw County, Michigan
2880' north and 440' west of southeast section corner
Forest Cover: red maple, red oak, bigtooth aspen, black oak
Stand Age (years): 59 Basal Area at Pit (ft^2 $acre^{-1}$): 90
Sampled By: Neil W. MacDonald

Pedon Description - Rubicon Block IV

A - 0 to 6 cm; N 2/0 loamy sand; weak fine granular structure; very friable; many fine and medium roots; abrupt wavy boundary (5410).

BE - 6 to 13 cm; 10YR 4/3 loamy sand; weak medium granular structure; very friable; many fine and medium roots; clear smooth boundary (5420).

Bs1 - 13 to 37 cm; 7.5YR 4/4 sand; weak coarse granular structure; friable; many fine, medium, and few large roots; 2% gravel; gradual smooth boundary (5430).

Bs2 - 37 to 70 cm; 7.5YR 4/6 sand; weak medium subangular blocky structure; friable; common fine and medium roots; 1-2% gravel; clear smooth boundary (5440).

BC - 70 to 133 cm; 10YR 5/6 sand; weak coarse granular structure; very friable; few medium roots; faint loamy sand band at clear smooth boundary (5450).

C - 133 to 190 cm; 10YR 6/6 sand; single grain; loose; few medium roots (5460). Auger sample indicated gravelly sand at 285 cm (not sampled).

Table B.31

Analytical Data - Rubicon Block IV

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
5410	5.8	1.123	-4.6	2.7	1343	444	603	498	568	492
5420	7.3	1.360	6.2	3.9	2122	956	1260	1278	1054	1351
5430	23.7	1.449	13.7	12.7	2472	1634	1454	2299	661	1372
5440	33.0	1.522	8.2	6.9	1517	823	580	1516	179	660
5450	62.7	1.590	5.2	4.0	1110	451	321	774	89	419
5460	56.8	1.625	2.2	1.1	895	285	139	520	88	379

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
5410	4.06	3.30	2.786	8.2	29.1	3.1	175.5	40.4	121.3
5420	4.84	4.22	.672	10.7	2.4	1.2	12.0	10.2	68.2
5430	5.14	4.52	.414	27.9	1.4	.5	11.1	6.3	32.4
5440	5.46	4.74	.201	33.2	1.4	.8	10.1	4.9	12.1
5450	5.74	4.96	.054	18.5	1.4	.9	8.0	3.8	4.7
5460	5.83	5.01	.027	19.2	1.1	1.1	5.8	3.6	3.0

Series: Rubicon Block: V Date Sampled: August 20, 1985
Location: Section 2, T24N R8W, Missaukee County, Michigan
350' north and 2380' west of southeast section corner
Forest Cover: white oak, red oak, and bigtooth aspen
Stand Age (years): 88 Basal Area at Pit (ft^2 $acre^{-1}$): 120
Sampled By: Neil W. MacDonald

Pedon Description - Rubicon Block V

A - 0 to 7 cm; 10YR 2/1 sand; weak medium granular structure; very friable; common fine and medium roots; clear smooth boundary (5510).

E - 7 to 18 cm; 10YR 6/2 to 10YR 5/3 sand; weak medium granular structure; very friable; common fine and medium roots; some mixing with A and Bs1 evident; clear wavy boundary (5520).

Bs1 - 18 to 34 cm; 7.5YR 4/4 sand; weak medium granular structure; very friable; common fine, medium, and large roots; <1% gravel; clear smooth boundary (5530).

Bs2 - 34 to 54 cm; 7.5YR 4/6 sand; weak medium subangular blocky structure; friable; common fine, medium, and large roots; <1% gravel; 5-10% ortstein in lower part; clear irregular boundary (5540).

BC - 54 to 100 cm; 10YR 6/4 sand; moderate coarse subangular blocky structure; friable to firm; 10-20% ortstein occurring in chunks in upper part; few fine and medium roots; clear smooth boundary (5550).

C - 100 to 166 cm; 10YR 7/3 sand; single grain; loose; few fine and medium roots; <1% gravel; few faint color bands at 130 and 165 cm (5560). Auger sample indicated similar non-effervescent sand to 330 cm (not sampled).

Table B.32

Analytical Data - Rubicon Block V

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
5510	6.5	1.203	-2.0	1.7	957	184	248	185	249	179
5520	11.0	1.469	.2	.2	620	90	80	49	111	132
5530	15.7	1.458	17.7	17.7	3318	2325	1883	3362	910	1883
5540	20.2	1.515	11.0	19.8	1811	1176	814	2241	271	1009
5550	45.7	1.634	3.4	8.8	722	421	187	1105	29	360
5560	66.0	1.649	1.4	1.6	496	225	73	426	43	256

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
5510	3.71	3.06	2.535	6.4	18.2	2.5	47.6	49.3	51.8
5520	4.07	3.60	.212	2.3	1.7	.9	4.1	5.0	36.8
5530	4.94	4.44	.616	13.6	1.5	.6	6.0	13.1	58.0
5540	5.06	4.67	.289	13.1	.8	.7	2.9	7.3	20.2
5550	5.08	4.88	.084	16.3	.2	.4	.9	3.1	6.6
5560	5.17	4.81	.015	13.9	.1	.6	.1	2.5	5.0

Series: Rubicon Block: VI Date Sampled: August 31, 1985
Location: Section 14, T20N R12W, Lake County, Michigan
2490' north and 2420' east of southwest section corner
Forest Cover: white oak and black oak
Stand Age (years): 88 Basal Area at Pit (ft^2 $acre^{-1}$): 120
Sampled By: Neil W. MacDonald, George M. MacDonald, and Douglas R. MacDonald

Pedon Description - Rubicon Block VI

A - 0 to 4 cm; 10YR 3/1 sand; weak fine granular structure; very friable; common fine and medium roots; clear smooth boundary (5610).

E - 4 to 11 cm; 10YR 4/2 sand; weak coarse granular structure; very friable; many fine and medium roots; clear wavy boundary (5620).

Bs1 - 11 to 35 cm; 7.5YR 4/6 sand; weak coarse granular structure; very friable; many fine and medium roots; gradual smooth boundary (5630).

Bs2 - 35 to 61 cm; 7.5YR 5/6 sand; weak medium granular structure; very friable; many fine and medium roots; clear smooth boundary (5640).

BC - 61 to 90 cm; 7.5YR 6/6 sand; weak medium subangular blocky structure; friable; few fine and medium roots; 5% weakly cemented ortstein; clear wavy boundary (5650).

C - 90 to 165 cm; 10YR 7/4 sand; single grain; loose; few fine and medium roots (5660). Auger sample indicated few faint 10YR 7/6 mottles at 245 cm; slight effervescence at 265 cm; strongly effervescent sand from 295 to 330 cm (not sampled).

Table B.33

Analytical Data - Rubicon Block VI

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
5610	3.5	1.134	-6.3	3.7	1034	200	343	220	329	229
5620	7.2	1.430	-2.2	1.8	911	176	312	237	282	263
5630	24.2	1.452	9.7	22.6	2375	1543	1276	1972	910	1739
5640	26.3	1.566	4.8	14.6	1504	817	547	1191	494	1150
5650	28.5	1.599	1.3	8.6	704	423	229	944	74	373
5660	75.3	1.599	.1	2.1	455	176	63	241	44	198

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL
5610	3.91	3.26	1.926	11.6	12.5	2.4	31.7	50.0	62.8
5620	4.09	3.52	.758	8.2	4.6	1.3	10.2	19.9	62.1
5630	4.86	4.48	.436	28.1	.8	.8	2.3	9.0	44.9
5640	4.85	4.51	.142	23.7	.5	.6	1.9	5.4	24.9
5650	4.94	4.76	.037	25.2	.2	.2	1.1	2.7	7.1
5660	5.11	4.87	.009	16.0	.2	.5	.2	2.3	2.7

Series: Spinks Block: I Date Sampled: June 27, 1985
Location: Section 21, T5N R1E, Shiawassee County, Michigan
2165' north and 610' east of southwest section corner
Forest Cover: black oak, white oak, and red maple
Stand Age (years): 53 Basal Area at Pit (ft^2 $acre^{-1}$): 140
Sampled By: Neil W. MacDonald and Doreen C. MacDonald

Pedon Description - Spinks Block I

A - 0 to 13 cm; 10YR 3/1 loamy fine sand; weak medium granular structure; very friable; many fine and medium roots; clear wavy boundary (6110).

E1 - 13 to 45 cm; 10YR 4/6 loamy fine sand; moderate fine subangular blocky structure; friable; common fine, medium, and few large roots; 2% gravel; gradual wavy boundary (6120).

E2 - 45 to 65 cm; 10YR 5/4 loamy fine sand; moderate medium subangular blocky structure; friable; few fine and common medium roots; 2% gravel; clear wavy boundary (6130).

E' & Bt - 65 to 136 cm; 10YR 5/4 loamy fine sand (E'); moderate medium subangular blocky structure; firm; few fine and medium roots; 2% gravel; abrupt wavy boundary (6140); and 7.5YR 4/4 fine sandy loam (Bt); moderate medium subangular blocky structure; firm; total 24 cm in bands; few fine and medium roots; abrupt smooth boundary (6150).

C - 136 to 159 cm; 10YR 5/4 fine sandy loam; moderate coarse subangular blocky structure; firm; few medium roots; strongly effervescent (6160).

Table B.34

Analytical Data - Spinks Block I

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
6110	12.5	1.065	-10.4	7.3	4293	929	1901	824	1537	907
6120	31.8	1.288	10.1	8.6	4565	1203	1147	1206	1023	1293
6130	19.5	1.423	6.3	4.9	3461	686	548	686	540	853
6140	47.3	1.440	2.7	2.1	3235	382	497	402	317	403
6150	24.3	1.657	-6.1	11.6	11026	1224	1394	638	139	113
6160	23.3	1.534	-36.7	29.9	4600	353	906	201	209	202

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL	CLAY
6110	5.31	4.76	3.668	20.6	130.4	1.0	911.0	68.8	8.7	-
6120	4.89	4.26	.450	12.7	5.4	2.0	28.9	11.7	71.7	7.6
6130	5.01	4.35	.145	5.3	4.7	1.5	16.5	9.2	44.1	7.5
6140	5.72	4.66	.066	3.7	20.3	2.2	41.7	7.5	12.5	3.5
6150	7.07	6.54	.134	2.5	221.9	15.0	677.3	25.9	.2	13.2
6160	8.35	7.92	.089	2.5	210.5	13.2	3505.1	12.2	.0	8.5

Series: Spinks Block: II Date Sampled: August 1, 1985
Location: Section 3, T1N R1E, Ingham County, Michigan
1340' south and 260' east of northwest section corner
Forest Cover: white oak, black oak, red maple, black cherry
Stand Age (years): 109 Basal Area at Pit (ft^2 $acre^{-1}$): 110
Sampled By: Neil W. MacDonald and Doreen C. MacDonald

Pedon Description - Spinks Block II

A - 0 to 4 cm; 10YR 3/2 loamy fine sand; moderate coarse granular structure; friable; many fine and medium roots; clear smooth boundary (6210).

E1 - 4 to 41 cm; 10YR 5/6 loamy sand; weak medium subangular blocky structure; very friable; common fine, medium, and large roots; 1-2% gravel; clear wavy boundary (6220).

E2 - 41 to 70 cm; 10YR 5/4 loamy sand; weak medium subangular blocky structure; friable; few fine and medium roots; 1% gravel; abrupt wavy boundary (6230).

E' & Bt - 70 to 210 cm; 10YR 5/4 loamy sand (E'); weak medium subangular blocky structure; friable; few medium roots; abrupt wavy boundary (6240); and 7.5YR 4/6 sandy loam (Bt); weak medium subangular blocky structure; firm; 45 cm total in bands and lamellae; few medium roots; abrupt wavy boundary (6250).

C - 210 to 232 cm; 10YR 5/3 loamy sand; massive; friable; few medium roots; faint depositional strata; strongly effervescent (6260).

Table B.35

Analytical Data - Spinks Block II

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
6210	3.8	1.173	-6.6	7.6	4138	646	1588	535	1497	548
6220	36.7	1.505	9.8	7.5	5301	846	1916	1080	1258	1404
6230	28.8	1.541	7.2	4.8	5140	465	1139	556	383	455
6240	95.3	1.432	2.6	1.2	5644	442	1242	312	251	226
6250	45.3	1.737	18.2	10.8	11369	1134	3699	950	292	334
6260	21.5	1.556	.5	1.4	3930	213	730	121	81	88

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL	CLAY
6210	3.92	3.30	3.694	20.4	40.6	4.6	95.6	66.6	151.3	-
6220	4.70	4.12	.306	29.1	4.3	6.4	10.3	20.4	94.3	7.8
6230	5.25	4.33	.088	13.0	20.0	6.6	32.2	14.0	28.9	3.7
6240	6.11	5.01	.096	10.3	22.0	2.6	181.0	9.6	1.3	3.7
6250	5.49	4.76	.076	6.8	113.6	7.0	683.7	61.3	11.9	13.9
6260	8.74	7.82	.092	1.8	65.7	4.0	3043.1	7.4	.0	2.6

Series: Spinks Block: III Date Sampled: August 2, 1985
Location: Section 10, T1N R5E, Livingston County, Michigan
2490' north and 1390' west of southeast section corner
Forest Cover: black oak, white oak, and shagbark hickory
Stand Age (years): 112 Basal Area at Pit (ft^2 $acre^{-1}$): 110
Sampled By: Neil W. MacDonald

Pedon Description - Spinks Block III

A - 0 to 11 cm; 10YR 3/2 loamy sand; moderate medium granular structure; very friable; many fine and medium roots; clear smooth boundary (6310).

E1 - 11 to 44 cm; 10YR 5/6 loamy sand; weak coarse granular structure; very friable; common medium and large roots; common worm channels filled with A horizon material; gradual smooth boundary (6320).

E2 - 44 to 75 cm; 10YR 5/4 loamy sand; weak coarse subangular blocky structure; friable; common medium roots; few worm channels; abrupt wavy boundary (6330).

E' & Bt - 75 to 223 cm; 10YR 5/4 sand (E'); weak medium subangular blocky structure; friable; few medium roots; 1% fine gravel; abrupt irregular boundary (6340); and 7.5YR 4/4 sandy loam (Bt); weak medium subangular blocky structure; firm; 45 cm total in bands and lamellae 0.5 to 10 cm thick; few medium roots; abrupt irregular boundary (6350).

2C - 223 to 241 cm; 10YR 5/4 sand; single grain; loose; few large roots; 10-15% gravel; moderately effervescent (6360).

Table B.36

Analytical Data - Spinks Block III

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
6310	10.7	1.174	-15.1	10.0	3339	634	1691	706	987	616
6320	33.2	1.493	3.0	1.7	3066	513	1054	690	595	662
6330	30.8	1.496	1.3	.6	2632	299	559	322	309	366
6340	103.3	1.555	.6	.6	2896	256	575	203	219	208
6350	45.3	1.735	3.0	2.4	7373	772	1479	620	211	162
6360	17.7	1.588	.0	.6	2764	213	510	117	193	273

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL	CLAY
6310	5.41	5.02	1.939	18.3	89.5	3.0	782.7	82.1	3.8	-
6320	5.25	4.37	.118	29.8	11.2	1.5	64.5	9.7	29.4	4.1
6330	5.87	4.73	.062	27.1	18.2	1.3	79.6	8.4	7.4	3.7
6340	6.15	4.97	.043	12.9	18.3	2.3	117.5	7.3	1.7	2.6
6350	6.13	5.23	.090	12.1	88.1	4.9	525.2	34.0	1.9	9.4
6360	8.79	7.85	.097	1.3	73.3	4.9	3438.5	14.0	.2	4.1

Series: Spinks Block: IV Date Sampled: August 6, 1985
Location: Section 20, T1S R3E, Washtenaw County, Michigan
1670' north and 1270' west of southeast section corner
Forest Cover: bur oak and red oak
Stand Age (years): 121 Basal Area at Pit (ft^2 $acre^{-1}$): 120
Sampled By: Neil W. MacDonald

Pedon Description - Spinks Block IV

A - 0 to 6 cm; 10YR 4/3 loamy fine sand; moderate medium granular structure; friable; common fine and medium roots; clear smooth boundary (6410).

E1 - 6 to 33 cm; 10YR 5/6 loamy fine sand; weak medium subangular blocky structure; friable; common medium and large roots; 1% gravel; gradual smooth boundary (6420).

E2 - 33 to 78 cm; 10YR 5/4 loamy sand; weak coarse subangular blocky structure; friable; common medium roots; 7-10% gravel and large cobbles; abrupt smooth boundary (6430).

E' & Bt - 78 to 202 cm; 10YR 5/4 sand (E'); weak medium subangular blocky structure; friable; few medium roots; <1% gravel; abrupt smooth discontinuous boundary (6440); and 7.5YR 4/4 sandy loam (Bt); moderate coarse subangular blocky structure; firm; 79 cm total, upper part of Bt almost continuous, grading into thin bands and lamellae; 5% gravel and cobbles; clear wavy boundary (6450).

C - 202 to 276 cm; 10YR 4/4 loamy sand; weak coarse subangular blocky structure; friable; few medium roots; few very faint bands or stains (6460). Auger sample indicated strongly effervescent sand below 276 cm (not sampled).

Table B.37

Analytical Data - Spinks Block IV

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
6410	5.7	.990	-10.5	8.1	4303	753	2079	738	1577	770
6420	26.5	1.416	5.1	7.4	4628	864	1552	784	1074	1240
6430	45.2	1.510	4.6	6.2	4297	622	898	624	604	893
6440	45.0	1.531	2.3	2.6	3978	337	927	199	335	309
6450	78.7	1.793	16.9	17.9	11416	1125	2095	956	119	192
6460	74.0	1.473	-1.0	1.6	3316	226	1027	149	257	197

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL	CLAY
6410	4.30	3.67	4.073	12.4	34.7	4.7	282.5	60.5	108.0	-
6420	4.63	4.01	.384	33.9	3.7	2.1	16.1	9.2	92.8	7.4
6430	4.76	4.09	.197	23.7	3.5	2.4	15.6	8.5	60.5	7.6
6440	6.16	5.11	.046	9.6	31.1	2.5	124.3	6.4	.8	3.3
6450	5.42	4.55	.062	4.0	167.6	4.9	479.1	53.4	17.3	14.0
6460	8.36	7.58	.017	8.0	44.9	2.7	1259.5	4.5	.0	1.6

Series: Spinks Block: V Date Sampled: August 27, 1985
Location: Section 22, T1S R9W, Kalamazoo County, Michigan
1880' north and 3070' west of southeast section corner
Forest Cover: black oak, white oak, and pignut hickory
Stand Age (years): 125 Basal Area at Pit (ft^2 $acre^{-1}$): 120
Sampled By: Neil W. MacDonald

Pedon Description - Spinks Block V

A - 0 to 17 cm; 10YR 3/2 loamy sand; weak medium granular structure; very friable; many fine and medium roots; 1% gravel; clear smooth boundary (6510).

E1 - 17 to 57 cm; 10YR 5/4 loamy sand; weak medium subangular blocky structure; very friable; common medium and fine roots; 1-2% gravel; few worm channels filled with A horizon material; clear wavy boundary (6520).

E2 - 57 to 88 cm; 10YR 6/4 sand; weak medium subangular blocky structure; friable; few fine and medium roots; 2-3% gravel; few faint loamy sand bands; abrupt wavy boundary (6530).

E' & Bt - 88 to 256 cm; 10YR 6/4 sand (E'); single grain; loose; common fine and medium roots; 2-3% gravel, occurring in thin bands in some spots; abrupt wavy boundary (6540); and 7.5YR 4/4 loamy sand to sandy loam (Bt); weak fine subangular blocky structure; friable; 28 cm total in 1-2 cm thick bands and lamellae; clear wavy boundary (6550).

C - 256 to 276 cm; 10YR 6/4 sand; single grain; loose; 2-3% gravel; strongly effervescent; bucket auger sample (6560).

Table B.38

Analytical Data - Spinks Block V

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
6510	16.7	1.189	-6.3	5.8	3480	1334	1206	1113	962	1408
6520	39.5	1.492	5.2	2.7	2831	703	858	753	589	962
6530	31.2	1.598	2.0	.8	2164	299	312	203	242	452
6540	140.2	1.600	1.3	.7	2711	288	537	300	290	366
6550	27.5	1.616	4.8	1.5	5459	647	1133	418	190	198
6560	20.0	1.571	-.9	.5	1429	91	341	82	114	145

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL	CLAY
6510	5.08	4.65	2.060	95.3	60.9	2.3	418.5	69.6	26.0	-
6520	5.02	4.27	.273	94.2	7.1	1.4	52.3	12.0	49.3	5.4
6530	5.83	4.66	.047	46.9	13.6	1.7	75.8	10.4	10.3	2.9
6540	5.95	4.89	.046	19.4	19.7	1.4	119.4	11.3	4.9	2.6
6550	6.06	5.14	.068	25.4	52.8	3.0	408.3	30.1	2.8	7.1
6560	8.89	7.85	.011	2.2	43.1	2.8	2264.8	6.0	.0	2.0

Series: Spinks Block: VI Date Sampled: August 30, 1985
Location: Section 18, T7S R12W, St. Joseph County, Michigan
935' south and 1600' west of northeast section corner
Forest Cover: black oak and sassafras
Stand Age (years): 53 Basal Area at Pit (ft^2 $acre^{-1}$): 70
Sampled By: Neil W. MacDonald and George M. MacDonald

Pedon Description - Spinks Block VI

Ap - 0 to 20 cm; 10YR 4/3 loamy sand; weak medium granular structure; very friable; many fine and medium roots; abrupt smooth boundary (6610).

E1 - 20 to 56 cm; 10YR 4/4 loamy sand; weak medium subangular blocky structure; friable; common fine, medium, and large roots; gradual smooth boundary (6620).

E2 - 56 to 98 cm; 10YR 5/4 loamy sand; weak coarse subangular blocky structure; very friable; common fine, medium, and large roots; clear wavy boundary (6630).

E' & Bt - 98 to 301 cm; 10YR 6/4 sand (E'); weak coarse granular structure; very friable; few fine and medium roots (6640); and 7.5YR 4/4 sandy loam (Bt); weak medium subangular blocky structure; friable; 29 cm total in bands 0.5 to 3.0 cm thick, approximately 10 cm between bands; abrupt smooth boundary (6650). Auger sample below 185 cm.

C - 301 to 351 cm; 10YR 6/4 sand; auger sample (6660).

Table B.39

Analytical Data - Spinks Block VI

SN	HT	BD	SADS	EXTS	DCFE	DCAL	AOFE	AOAL	NPFE	NPAL
6610	19.5	1.415	5.9	5.5	3341	1143	1496	1291	916	1462
6620	35.5	1.528	8.3	4.2	3133	719	1014	963	716	1342
6630	42.0	1.544	6.8	2.8	2560	510	653	587	474	998
6640	173.7	1.566	2.8	1.1	2114	225	350	201	202	378
6650	29.3	1.652	7.7	2.7	5156	557	1692	660	191	203
6660	50.0	1.492	1.1	2.2	1465	168	446	131	156	221

SN	PH2O	PHCA	%ORGC	EXTP	EXMG	EXNA	EXCA	EXK	EXAL	CLAY
6610	5.02	4.23	.472	96.2	8.7	1.0	40.2	24.6	74.4	-
6620	5.34	4.39	.062	79.4	8.1	.6	27.5	17.1	34.7	4.5
6630	5.54	4.45	.029	49.3	9.9	1.0	41.8	8.8	29.0	3.0
6640	5.77	4.62	.021	14.2	9.8	1.5	78.3	6.2	8.5	2.0
6650	5.95	5.20	.065	14.8	87.4	4.9	398.1	28.1	7.2	8.4
6660	6.51	5.50	.009	8.2	10.8	1.4	68.8	5.9	.0	1.4

APPENDIX C

APPENDIX C

DESCRIPTION OF ANALYTICAL BULK SAMPLE

As an internal quality control check, a bulk soil sample was included in analyses as described in Chapter IV, Materials and Methods. The bulk sample used was a composite sample from the Bw1 horizon of a Graycalm-Montcalm soil complex supporting a 70-year-old mixed red, white, and black oak stand located in Section 26, T32N R2E, Montmorency County, Michigan. Soil samples were obtained with soil sampling probes from 90 randomly located points within a 13.6 hectare area as part of a separate research project. Soil was air-dried, passed through a 1 mm sieve, and thoroughly mixed prior to analysis.

Table C.1

Analytical Bulk Sample Statistics

Property†	Units	Mean	S.D.‡	Range	C.V.††	n
SO_4-S Adsorbed	mg kg^{-1}	3.5	0.4	3.1-4.2	10.1%	12
Extractable S	mg kg^{-1}	6.8	0.3	6.5-7.3	4.3%	8
Extractable P	mg kg^{-1}	32.2	2.3	28.3-34.4	7.1%	12
DC-Fe	mg kg^{-1}	2262	115	2034-2443	5.1%	11
DC-Al	mg kg^{-1}	888	37	820-935	4.2%	12
AO-Fe	mg kg^{-1}	1243	85	1107-1364	6.8%	12
AO-Al	mg kg^{-1}	1240	133	1063-1415	10.7%	12
NP-Fe	mg kg^{-1}	902	57	789-1008	6.3%	12
NP-Al	mg kg^{-1}	1155	64	992-1273	5.5%	12
Exch Al	mg kg^{-1}	36.5	3.6	32.4-39.0	9.9%	3
Exch Ca	mg kg^{-1}	54.6	1.4	52.6-57.5	2.6%	12
Exch Mg	mg kg^{-1}	7.3	0.4	6.7-7.9	5.2%	12
Exch K	mg kg^{-1}	15.8	0.9	14.2-18.0	5.4%	12
Exch Na	mg kg^{-1}	22.1	1.8	19.1-25.5	8.1%	12
Organic Carbon	%	0.40	0.05	0.32-0.50	12.9%	14
pH-H_2O	$-Log(H^+)$	4.99	0.01	4.97-5.01	0.25%	12
pH-$CaCl_2$	$-Log(H^+)$	4.42	0.02	4.39-4.44	0.35%	12

† Soil Property DC = Dithionite-Citrate Extraction
AO = Ammonium Oxalate Extraction
NP = Sodium Pyrophosphate Extraction
Exch = Exchangeable

‡ S.D. = Standard Deviation

†† C.V. = Coefficient of Variation, calculated from unrounded mean and standard deviation values.

APPENDIX D

APPENDIX D

ANALYSIS OF VARIANCE TABLES NOT INCLUDED IN TEXT

Table D.1

Analysis of Variance Results:
Soil Preparation x SO_4-S Concentration Interactions†

A Horizon - Montcalm Loamy Sand

Source	DF	SS	MS	F	P
Block	2	0.1905	0.0952	3.25	0.059
Soil Preparation	1	2.9165	2.9165	99.62	0.000
SO_4-S Concentration	5	5.5049	1.1010	37.61	0.000
SP x SC	5	2.8949	0.5790	19.78	0.000
Error	21‡	0.6148	0.0293		

E Horizon - Montcalm Loamy Sand

Source	DF	SS	MS	F	P
Block	2	0.2166	0.1083	1.28	0.298
Soil Preparation	1	3.0759	3.0759	36.37	0.000
SO_4-S Concentration	5	6.5534	1.3107	15.50	0.000
SP x SC	5	0.4804	0.0961	1.14	0.369
Error	22	1.8605	0.0846		

‡ One degree of freedom subtracted due to deletion of anomalous Block 3, field-moist, 100 mg S L^{-1} datum.

Table D.1 (continued)

Bs Horizon - Montcalm Loamy Sand

Source	DF	SS	MS	F	P
Block	2	0.0569	0.0285	2.93	0.074
Soil Preparation	1	1.3205	1.3205	135.96	0.000
SO_4-S Concentration	5	11.0338	2.2068	227.21	0.000
SP x SC	5	0.0799	0.0160	1.65	0.189
Error	22	0.2137	0.0097		

E' Horizon - Montcalm Loamy Sand

Source	DF	SS	MS	F	P
Block	2	0.0783	0.0392	0.43	0.656
Soil Preparation	1	0.4343	0.4343	4.82	0.039
SO_4-S Concentration	5	11.5394	2.3079	25.62	0.000
SP x SC	5	1.5570	0.3114	3.46	0.019
Error	22	1.9822	0.0901		

Bt Horizon - Montcalm Loamy Sand

Source	DF	SS	MS	F	P
Block	2	1.2242	0.6121	3.50	0.048
Soil Preparation	1	0.0690	0.0690	0.39	0.539
SO_4-S Concentration	5	41.6539	8.3308	47.60	0.000
SP x SC	5	1.4580	0.2916	1.67	0.184
Error	22	3.8498	0.1750		

Table D.1 (continued)

C Horizon - Montcalm Loamy Sand

Source	DF	SS	MS	F	P
Block	2	1.7879	0.8939	1.42	0.263
Soil Preparation	1	19.5502	19.5502	31.13	0.000
SO_4-S Concentration	5	10.2073	2.0415	3.25	0.024
SP x SC	5	11.1971	2.2394	3.57	0.016
Error	22	13.8165	0.6280		

† Data statistically analyzed as (+,-) ln(|mg S kg^{-1}|+1), a negative sign denoting numbers below zero on the original scale of measurement.

Table D.2

Analysis of Variance Results:
Kalkaska and Grayling Preliminary Study†

Source	DF	SS	MS	F	P
Block	2	0.4286	0.2143	1.37	0.263
Series	1	8.4201	8.4201	53.92	0.000
Soil Preparation	1	0.9422	0.9422	6.03	0.016
Soil Horizon	2	9.5999	4.7999	30.74	0.000
SO_4-S Concentration	1	10.0586	10.0586	64.41	0.000
S x SP	1	0.5228	0.5228	3.35	0.069
S x SH	2	20.9411	10.4706	67.05	0.000
S x SC	1	0.0076	0.0076	0.05	0.787
SP x SH	2	1.3670	0.6835	4.38	0.017
SP x SC	1	0.5833	0.5833	3.74	0.055
SH x SC	2	0.1172	0.0586	0.38	0.686
Error‡	55	8.5892	0.1562		

† Data statistically analyzed as (+,-) ln(|mg S kg^{-1}|+1), a negative sign denoting numbers below zero on the original scale of measurement.

‡ Three and four way interactions were non-significant and were pooled with error.

Table D.3

Analysis of Variance Results:
Sulfate Adsorption within Soil Series†

Grayling Series

Source	DF	SS	MS	F	P
Block	5	0.7279	0.1456	1.17	0.36
Soil Horizon	4	70.8361	17.7090	141.94	0.00
Error	20	2.4953	0.1248		

Rubicon Series

Source	DF	SS	MS	F	P
Block	5	5.3336	1.0667	4.10	0.01
Soil Horizon	5	84.3859	16.8772	64.91	0.00
Error	25	6.5006	0.2600		

Kalkaska Series

Source	DF	SS	MS	F	P
Block	5	0.5797	0.1159	1.48	0.23
Soil Horizon	5	59.2259	11.8452	151.08	0.00
Error	23	1.8033	0.0784		

Montcalm Series

Source	DF	SS	MS	F	P
Block	5	3.4360	0.6872	2.33	0.07
Soil Horizon	6	50.6777	8.4463	28.65	0.00
Error	23	6.7806	0.2948		

Table D.3 (continued)

Spinks Series‡

Source	DF	SS	MS	F	P
Block	5	8.7333	1.7467	3.04	0.03
Soil Horizon	5	62.1340	12.4268	21.61	0.00
Error	23	13.2253	0.5750		

Oshtemo Series

Source	DF	SS	MS	F	P
Block	5	8.0984	1.6197	2.50	0.06
Soil Horizon	5	51.2671	10.2534	15.85	0.00
Error	24	15.5248	0.6469		

† Data statistically analyzed as (+,-) $\ln(|mg\ S\ kg^{-1}|+1)$, a negative sign denoting numbers below zero on the original scale of measurement.

‡ Spinks Block I Bt and C horizon data excluded from analysis.

Table D.4

Analysis of Variance Results:
Extractable Sulfate within Soil Series†

Grayling Series

Source	DF	SS	MS	F	P
Block	5	2.2717	0.4543	6.32	0.00
Soil Horizon	4	10.2841	2.5710	35.75	0.00
Error	20	1.4383	0.0719		

Table D.4 (continued)

Rubicon Series

Source	DF	SS	MS	F	P
Block	5	2.3038	0.4608	2.36	0.07
Soil Horizon	5	18.7310	3.7462	19.18	0.00
Error	25	4.8836	0.1953		

Kalkaska Series

Source	DF	SS	MS	F	P
Block	5	6.4487	1.2897	4.69	0.00
Soil Horizon	5	5.6552	1.1310	4.11	0.01
Error	23	6.3236	0.2749		

Montcalm Series

Source	DF	SS	MS	F	P
Block	5	2.4477	0.4895	3.15	0.03
Soil Horizon	6	5.3673	0.8945	5.76	0.00
Error	23	3.5705	0.1552		

Spinks Series‡

Source	DF	SS	MS	F	P
Block	5	5.1970	1.0394	8.50	0.00
Soil Horizon	5	9.0884	1.8177	14.86	0.00
Error	24	2.9364	0.1224		

Table D.4 (continued)

Oshtemo Series

Source	DF	SS	MS	F	P
Block	5	8.8287	1.7657	10.76	0.00
Soil Horizon	5	7.3912	1.4782	9.00	0.00
Error	24	3.9402	0.1642		

† Data statistically analyzed as $\ln(|mg\ S\ kg^{-1}|+1)$.

‡ Spinks Block I C horizon data excluded from analysis.

Table D.5

Analysis of Variance Results:
Inter-Series Comparison of Sulfate Adsorbed in Upper 150 cm†

Source	DF	SS	MS	F	P
Block	5	191.2659	38.2532	1.69	0.18
Soil Series	5	27.5354	5.5071	0.24	0.94
Error‡	24	543.4844	22.6452		

† Data analyzed as g $S.m^{-2}$ to 150 cm in sulfate-adsorbing horizons (g S 1.5 m^{-3}).

‡ Spinks Block I data excluded from analysis.

Table D.6

Analysis of Variance Results:
Extractable Sulfate Contents to 150 cm by Soil Series†

Source	DF	SS	MS	F	P
Block	5	0.8791	0.1758	1.83	0.14
Soil Series	5	2.3096	0.4619	4.80	0.00
Error	25	2.4072	0.0963		

† Data analyzed as log (g S m^{-2}), calculated to 150 cm from top of A horizon.

Table D.7

Analysis of Variance Results:
Extractable Sulfate Contents to 150 cm by Geographic Region†

Source	DF	SS	MS	F	P
Geographic Region	2	1.0202	0.5101	3.68	0.04
Error	33	4.5756	0.1387		

† Data analyzed as log (g S m^{-2}), calculated to 150 cm from top of A horizon.

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