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OXIDATION - REDUCTION STUDIES ON THE MECHANISM OF B HORIZON FORMATION IN PODZOLS

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Lloyd J. McKenzie

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Major professor

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OXIDATION-REDUCTION STUDIES ON THE MECHANISM OF B HORIZON FORMATION IN PODZOLS

By

Lloyd J. McKenzie

A THESIS

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ABSTRACT

Oxidation-reduction potentials *in situ* have been measured over a period of two years at various depths in a hydrosequence of soils. The well drained soil studied was Kalkaska sand, the imperfectly drained soil was Saugatuck sand, and the poorly drained soil was Roscommon sand. The distribution of certain microorganisms in the soil profile of the Kalkaska and Saugatuck sands was also studied.

Variations in redox potential with time were observed to correlate with the soil moisture content and with temperature; variations in redox potential with space were observed to correlate with soil horizons. The population of the ferric citrate oxidizing organisms decreased with depth and filamentous, sheathed bacteria resembling *Sphaeratilus* species known to be active in oxidation of ferrous to ferric iron were isolated from the B_{ir} horizons of the Kalkaska and Saugatuck sands.

Evidence is given of possible mechanisms of mobilization of iron oxides in the A horizon and precipitation of ferric hydroxide in the B horizon of podzol soils.

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INTRODUCTION

Oxidation and solution are two chemical processes that are involved in soil genesis. There is a differential solubility in the oxidized and reduced state for several of the metallic ions such as iron and manganese in soils. For example, ferrous hydroxide is a million times more soluble than ferric hydroxide. Recently, McKenzie and Erickson (49) have reported results of studies on the oxidation status of soils by horizons which indicated that such elements as iron and manganese could be mobilized in the A horizon, translocated into the B horizon, and there precipitated due to a change in oxidation-reduction status within the soil profile. The present study is a continuation of the work in which a more detailed study of a hydrosequence of soils has been carried out.

Oxidation-reduction potentials have now been studied in the horizons of a hydrosequence of soils over a period of time using an adaptation of the technique developed by Quispel (65) and used by McKenzie and Erickson (49). Measurements were made from September 9, 1953 to August 10, 1955 in all seasons of the year. The results were treated statistically to determine significant variations in the oxidation reduction potentials observed.

Mechanical analyses and mineralogical analyses were also carried out. In addition, a special sampling was carried out designed to isolate iron oxidizing microorganisms from the soils under study and to gain some information about the ability of soil organisms present in the soils to utilize organic complex forming compounds as a source of energy.

REVIEW OF LITERATURE

Marbut (43) discussed the early theories on the development of Podzols. One theory assumed that iron was immediately converted to ferric oxides on decomposition of the minerals in the A horizon. Soil solutions containing acid organic matter reduced the ferric oxide to ferrous oxide and formed organic acid-ferrous oxide complexes which were relatively more soluble than the ferric oxide. These complexes were translocated in the leaching waters to lower regions in the soil. At relatively shallow depths the organic acid complex was decomposed by oxygen and the ferrous iron on being released was re-oxidised to ferric oxide and precipitated.

In 1910, Dr. Albert (1,2) in Germany studied the genesis of Podzols. He reported that the cementing material between the soil particles consists largely of clay-iron phosphate complexes. Humus materials may not play an essential role in podzol formation because podzols may form without humus materials. Dr. Albert showed there was no variation in aeration within the profile and correlated "ortstein" formation with depth of penetration of summer rains.

Gillespie (27) about 1920 was one of the first investigators to work with oxidation-reduction potentials in soils. In laboratory studies he found that soils became highly reduced when subject to waterlogging. This reduced condition was intensified by the addition of dextrose. The increase in intensity of reduction was accompanied by a foul odor. He discussed the significance of reducing conditions and of reduction potentials in soil study.

In 1914, Morison and Sothers (54) studied the formation of iron pan. They reported that peat was a strong reducing agent but was not capable of reducing ferric oxide to ferrous oxide and that the solution obtained by the action of peat on ferric oxide does not contain ferrous humate which appears to be accompanied by the presence of ferrous ions. Peat in the presence of water removes considerable quantities of minerals such as ferric oxide, calcium oxide, and aluminum oxide from the soil as colloidal suspensions. These colloid sols are not very sensitive to changes in concentration but evaporation to dryness destroys their capacity for suspension to some extent. In the case of iron the compound formed is probably ferric humate, but may be an adsorption complex of colloidal humus and colloidal ferric hydroxide. They supported the theory that the pan formation in Podzols was due to the formation of colloidal humus compounds of aluminum and iron which are carried down into the soil and there precipitated by soluble salts, loss of water or by a change of bases.

At the same time, Morison and Doyne (53) studied the method of extracting iron from soils. They concluded that the known methods were unsatisfactory for the determination of ferrous iron in soils, and that the occurence of large amounts of ferrous and ferric iron in the soluble state in the soil was highly improbable.

In 1922, Neller (56) reported that growing green plants accelerated the oxidation processes in soils. He measured the increase in carbon dioxide produced in planted cultures above that produced in unplanted cultures and found it to vary for different plants. Working with buckwheat, field beans, and soy beans he found that a second crop was more effective than the first crop.

About the same time Bouyoucos (15) reported that different chemical agents had decidedly different effects on the oxidation of iron both as to rate and extent. The non-oxidizing effect of some reagents could dominate the oxidizing effect of others; and the effect could be observed in the absence of oxygen from the air.

In the late 1920's and early 1930's several important investigators did much to develop the theory of oxidation-reduction potentials. These were Clark and his co-workers (21), Remesow (66), and Michaelis (52) who published a discussion of the theory of oxidation and reduction in 1930.

In 1927, Halvorson and Starkey (29) developed a theory of equilibrium for ferrous and ferric iron when present in both the solid and soluble form. They showed that as pH increases ferrous iron will tend to be converted to ferric iron and to precipitate as ferric hydroxide. However if the pressure of oxygen varies, then as the pressure is reduced, ferric hydroxide will tend to go into solution and ferric iron will be reduced to ferrous iron. If complex ions are formed, then ferrous iron will be removed from solution, and the tendency will be for more ferric hydroxide to go into solution. If there are enough complex ions formed it is possible to keep much larger quantities of iron in solution even at low hydrogen ion concentrations then would be normal if no complexes were formed.

In 1927, Starky and Halvorson (76) studied the effect of microorganisms on the precipitation of iron in soils. Some of the means by which iron may be precipitated were listed as follows:

(1) The activity of iron bacteria.

(2) The activity of heterotrophic microorganisms decomposing organic compounds of iron.

(3) Activities of organisms causing changes in oxygen pressure or reaction and thereby precipitating iron.

(4) Strictly chemical changes as a result of changes in environment.

They concluded that microorganisms could be responsible for both the reduction and solution of iron or its precipitation, either directly or indirectly by decomposing the organic radical of complex organic compounds of iron. However iron could be brought into solution in a number of ways, some of which were not related to microorganisms. Therefore it was necessary to understand more thoroughly the reactions responsible for changes in the form of iron in the soil before biological changes would have any significance.

In 1930, Tenney and Waksman (80) studied the decomposition of chemical constituents of organic materials under anaerobic conditions. They reported that in general, anaerobic decomposition was slower than aerobic decomposition. In all cases there was a net gain in protein and in some cases there was a net gain in lignin under anaerobic decomposition. Under aerobic conditions, decomposition proceeded completely to the production of CO_2 and water, while under anaerobic conditions more alcohols and organic acids were produced. With oak leaves, under aerobic conditions, much of the protein was decomposed with production of ammonia which escaped into the air; while under anaerobic conditions, less protein was decomposed and losses in ammonia were also lower.

In 1930, Smythe and Schmidt (73) studied the mode of combination of iron with a number of organic complex forming compounds. They studied the equilibrium between ammonium thiocyanate and ferric iron (Ferric iron complexes are more stable towards oxidation and decomposition than the ferrous iron complexes), the stability of the iron compounds to acid and alkali, and the migration of the iron under the influence of an electric current. Their results suggested that iron could form stable complexes (undissociated compounds) with organic materials which possessed a particular grouping within the molecule. The following classes of substances were cited as having this particular grouping: hydroxymonocarboxylic acids (lactic, gluconic); dicarboxylic acids (oxalic, malonic); hydroxydicarboxylic and hydroxytricarboxylic acids (tartaric, citric); amino acids which are also hydroxy or dicarboxylic acids (aspartic, serine); certain inorganic acids (phosphoric, arsenic); certain phosphorus containing compounds (nucleic acid, glycerophosphoric acid); and certain proteins (casein, gelatin). They found a correlation of the amount of iron bound by casein and gelatin with certain groupings which were known to occur in the molecules of those proteins. They explained the combination of iron with the organic molecules on the basis of the residual charge of the atoms.

In 1930, Mattson (45) reported on a study of the laws of soil colloidal behavior. Using cataphoresis methods, colorimetic pH measures and chemical methods for determination of the reacting components, he characterized a number of soil colloidal materials including silica, sesquioxides, humus and humates of iron and aluminum. Silica and humus are electro-negative. The sesquioxides are electrical ampholytes, that is, they are electro-positive in acid solution and electro-negative in alkaline solution. The position of the isoelectric point depends on the nature of the acid anion. The sesquioxides also adsorb both acids and bases.

The alkali humates are highly dispersable. They may form true solutions. Humates of divalent cations are less easily dispersed. Aluminum and ferric humates are amphoteric. They are non-dispersable at the isoelectric point but are increasingly dispersable above or below the isoelectric point with increasing negative or positive charge. He also showed that ferric hydroxide is isoelectric at pH 7.1 and that aluminum hydroxide is isoelectric at pH 8.1. However, complexes of ferric hydroxide and phosphate and aluminum hydroxide and phosphate and also silicates are isoelectric at much lower pH's so that such complexes could be precipitated isoelectrically under conditions normally found in soils.

In a further study in 1931, Mattson (46) showed that ferric humates are isoelectric at pH 4.8-7.0 depending on the humus sesquioxide ratio. In addition, aluminum humates are isoelectric at pH 4.8-8.0 depending on the humus-sesquioxide ratio. He also found that the clay colloids reacted with aluminum and iron forming isoelectric precipitates in the same manner as the humus complex. In another report in the same year, Mattson (47) described the colloidal behavior of the soil ampholytes. He found that soil colloids in which the silica-sesquioxide ratio was low showed a pronounced amphoteric behavior in the normal pH range of soils. When the ratio is large, the soil colloids do not react in the normal pH range in soils. All soil colloids react amphoterically with phosphates. The isoelectric point is not constant but varies with the dissociation of the compounds formed by the colloid with the adsorbed ions. The soil colloids react as acids above the isoelectric pH and as bases below the isoelectric pH. Mattson calls the transition point "the point of exchange neutrality." This point is not fixed for the colloid but varies with the energy of displacement of the anions and cations for the hydroxyl and hydrogen ions in the electrodialized free ampholytoid.

Again in 1931, Mattson (48) reported on the colloidal behavior of a number of proteins. They were found to be isoelectric at pH 4.8-5.2. Iron and aluminum hydroxides are isoelectric at pH 7.1 and 8.1, respectively. A mixture of aluminum or iron with protein was isoelectric at some point between pH 7.1-8.1 and pH 4.8-5.2 depending on the relationship between the charge and relative concentration of the colloids. The mixture was isoelectric at the pH where the total charge ratio was equal to 1. This could vary depending on the relative concentrations of the charged colloids. The protein complexes that were formed (aluminum and ferric proteinates, protein humates, bentonites and silicates) all obeyed the fundamental principle of the colloidal behavior previously described.

In 1931, Smythe (72) studied the relative ease of oxidation of ferrous iron in the ionic form by oxygen of the air as compared to the unionized ferrous hydroxide in alkaline solution, or to the complexes that could be formed with an organic anion. He showed that ferrous iron was more readily oxidized as the complex or as the unionized ferrous hydroxide in alkaline solution and that this oxidation could take place regardless of the reaction of the solution. He discussed the catalytic effect of ferrous and ferric iron in certain oxidations and gave an interpretation of the mechanism involved.

In the same year Michaelis and Smythe (51) studied the relationship between rate of oxidation and the property of autooxidation of iron systems. Since the more negative the potential of the system, the more highly autooxidizable it is, there should be a relation between the rate of oxidation of an iron system and its potential. They measured the rates of oxidation of a number of iron complex systems and found there was a relationship between rate of reaction and potential. Those complexes with the lowest potential were most readily oxidized. On the basis of these observations they were able to correct the potential of an iron system which had been reported by another investigator.

In 1931, Halvorson (28) studied equilibrium conditions for iron solutions under the influence of atmospheric oxygen and carbon dioxide and developed equations to express the conditions. He considered the activities of microorganisms associated with solution and precipitation as well as with oxidation and reduction of iron in relation to the equations developed. He observed several important points. Under anaerobic conditions, heterotrophic organisms could dissolve metallic iron. They could also dissolve and reduce ferric hydroxide. Such changes could take place from a decrease in oxygen pressure and the formation of acid; and could occur even at reactions close to neutrality. Ferrous carbonate could be precipitated under anaerobic conditions when carbon dioxide was increased as a result of organic matter decomposition. The activity of iron bacteria appears to occur only under environmental conditions favorable to spontaneous oxidation by chemical agencies. The solution and precipitation of iron in nature are associated with equilibrium conditions which depend on oxygen tension, carbon dioxide tension, acidity, and the presence of organic compounds. These conditions may be modified extensively by microorganisms. The activities of iron bacteria are confined solely to its precipitation. Halvorson thinks that their activities have been overemphasized at the expense of the heterotrophic bacteria.

In 1932, Willis (87) using Dunbar fine sandy loam, devised a method for determining the E_h-pH relationship of the soil. He used a nitrogen atmosphere. He found an inverse relationship between E_h and pH, and estimated there was about 60 millivolts change in E_h for each pH unit change.

Bradfield et al (17) studied the oxidation-reduction state of the soil in relation to the production of fruit in 1934. They found that they could eliminate 80 to 90 percent of the low yielding trees in apple orchards on the basis of the low oxidation-reduction potentials observed in the spring. The low potentials tended to disappear in the summer months. They noted a general agreement with Willis' work on the E_h-pH relationship. That is, there was a generally linear relationship between E_h and pH except at low pH's but they believed that 80 millivolts per pH unit was a more probable factor. They used quinhydrone in 0.05 molar potassium acid phthallate as a reference solution for standardizing electrodes. Electrodes which failed to indicate a pH value of 3.98 ± 0.05 were disqualified for redox potential measurements. The potentials obtained in soils had to be constant and had to be reproducible on more than one electrode before they could be accepted with confidence. Soil redox potentials may never prove to be absolutely exact, but for practical purposes they were sufficiently reproducible to merit consideration. They also studied the effect of past history of the platinum electrodes on the redox potentials obtained. It was found that the electrodes were affected by past treatment but that the effect disappeared after a short time. This had the effect of delaying the electrode in coming to equilibrium with the soil in which it was placed. Subsequent readings agreed well with untreated fresh electrodes once equilibrium was reached. The use of a vacuum tube potentiometer eliminated the possibility of polarization of the electrodes when measurements were made. One tenth normal H_2SO_4 was used as the suspension medium. It was claimed that the H_2SO_4 medium was practically similar to the water suspension medium but was better poised. The acid medium inhibited the action of the microorganisms and shortened the time required for the electrodes to reach equilibrium with the soil solution. However, if proper time was allowed for equilibrium to be reached, and the electrodes were properly cleaned so as not to be affected by past history, water could be used to advantage as a suspension medium. There was no apparent difference in redox measurements resulting from different ratios of soil to suspension medium. Therefore a standardized volume sample was used. The E_h value of the soil was calculated by adding 0.250 volts to the value obtained from the soil when the sample was measured against the standard saturated calomel electrode. It represented the soil potential referred to the standard hydrogen electrode.

At the same time Brown (18) reviewed the principles involved in the study of soils by means of oxidation-reduction potentials. He used a rapid method of measuring E_h in the laboratory and developed the method of preparing electrodes which were later used by Quispel (65), Lemon and Erickson (40) and McKenzie and Erickson (49).

In 1934, Heintze (30) used the glass electrode instead of the calomel electrode as the reference electrode to minimize polarization and to facilitate instantaneous E_h-pH measurements. She used water as the suspension medium and reported that the ratio of soil to water was of little importance in the measurement of redox potentials. She also claimed that the presence of air or nitrogen did not effect the potential. Soils that contained readily decomposable organic matter dropped rapidly in potential on being waterlogged; but soils that contained little organic matter tended to resist any drop in E_h. Heintze recommended that E_h and pH of soils should not be considered separately since the E_h of a soil depended greatly on the pH.

In 1934, Kohnke (35) reported that the oxygen supply of a soil determines the oxidation-reduction potential. A high potential is indicative of a well drained and oxidized soil and a low potential is indicative of a poorly drained de-aerated soil. The principal substances entering into the oxidation-reduction reactions of soils are colloidal clay, organic substances and humus, and compounds of iron and managanese. He used 59 millivolts as the correction for the E_h per pH unit. Aeration increased the potential and waterlogging lowered the potential. Surface soil horizons gave lower potentials than subsurface or subsoil horizons in the spring. This difference tended to disappear during the summer. Quantitative determinations gave large and significant differences between well and poorly aerated soils. He reported a large experimental error.

In the same year Peech and Batjer (59) made a critical study of the methods used in measuring oxidation-reduction potentials of soils. They used shiny platinum electrodes and found that cleaning with chromic acid tended to give high results; but when the chromic acid treatment was followed by rinsing in alcohol and flaming to dull red heat, the high results were not obtained. They reported that the use of a vacuum tube potentiometer eliminated polarization of electrodes. They used a sulphuric acid suspension medium because the redox systems were better poised in H_2SO_4; and suggested that a nitrogen atmosphere be used when water was used as the suspension medium. They used the factor of 80 millivolts for correcting E_h measurements for pH. They reported that little reduction occurred in soils in the spring until the temperature had reached 55°F.

In 1936, Sturgis (79) reported that low potentials in waterlogged soils were caused by decomposition of fresh organic matter.

The solubility of phosphorus was reduced under conditions causing low potentials in soils. In the absence of actively decomposing organic matter, large amounts of iron compounds precipitated around the roots of rice plants. The presence of gypsum in a waterlogged soil caused the production of sulphides which reduced rice yields. The application of leguminous organic matter tended to increase rice yields. He reported potentials as low as 80 millivolts in soils containing actively decomposing organic matter.

In the same year Darnell and Eisenmenger (22) found that there was little or no change in potential with the addition of fertilizers containing nitrogen. The changes correlated better with changes in pH. They reported a rapid fall in potential when fresh organic matter underwent rapid decomposition and gave a rapid depletion of oxygen as the cause.

In 1936, Burrows and Cordon (20) reported that the type of decomposable organic matter was an important factor in the determination of the reducing intensity that prevailed. They reported that casein decomposition resulted in highly positive potentials while carbohydrate decomposition resulted in negative potentials not unlike those produced in soils. They also reported that moisture did not greatly affect potentials.

In the same year Willis (86) discussed the importance of oxidation-reduction potentials of soils in soil fertility. He pointed out that manganese deficiency caused by overliming could be explained by consideration of E_h as well as pH. He also stated that two soil components, oxygen and organic matter, appeared to govern the oxidation-reduction equilibrium in the soil. Both required activation, the former by catalysis and the latter by microorganisms. He suggested evidence that phosphorus, potassium, copper, manganese, boron, silicic acid, organic matter, pH, aeration, and temperature are to some degree interdependent variables.

In 1938, Stevenson et al (78) working with Oregon soils found that different soil types under field conditions showed little variation in oxidation-reduction potential by the methods used. There was little variation in potential between horizons even when there was a tight subsoil. They reported that fresh organic matter alone did not cause a fall in potential, but waterlogging caused a rapid fall in potential. They reported that oxidation-reduction potentials were not reliable indicators of anaerobic conditions in the soil.

In 1939, Buehrer et al (19) found that the E_h-pH relationship could be determined by simply diluting a soil suspension with water. They showed that the E_h change amounted to about 68 to 70 millivolts per unit change in pH, and that bubbling nitrogen through the soil tended to lower the E_h value. Puddling caused a drop in E_h which they believed was due to factors other than oxygen depletion. An abundance of oxygen tended to increase the E_h. The addition of alfalfa to a soil suspension caused a marked decrease in E_h which was taken to be indicative of the nature of the reduced compounds formed during its decomposition.

Volk (83), working with Alabama soils, did much to establish a standardized technique for the measurement of oxidation-reduction potentials in the laboratory. Batjer, Bradfield, Kohnke, and Peech all used N/10 H_2SO_4 as the suspension medium to inhibit microbial activity and to add poise to the redox system. Volk claimed that sulphuric acid dissolved materials in the soil which were not ordinarily active and therefore acid suspensions and water suspensions were not comparable. Only Kohnke and Willis used a nitrogen atmosphere, while others (17, 30, 59) disregarded the effect of oxygen entirely. Volk reported that arable soils changed little in E_h with treatment but that reduced soils were rapidly oxidized unless oxygen was expelled with nitrogen. He reported that all preservatives used to inhibit microbiological activity changed the E_h of the soil. Volk cooled all samples to a point just above freezing, used boiled water saturated with nitrogen as the suspension medium, and performed all analysis in a nitrogen atmosphere. He also reported that potential drift was due to the past history of the electrode. Wire electrodes were superior to foil electrodes. In a second paper (81) he reported the results of extensive studies on Alabama soils. He found that cultivated soils in general, had higher E_h values than virgin soils in the 0 to 8 inch depth, but that subsoils were similar. He found little difference in soil types. Differences rarely exceeded fifty millivolts which he did not think important since they could have been due to differences in soil material rather than state of oxidation. Swampy soils often had higher E_h values than did well drained upland soils. After rains the E_h tended to rise for a time due to the oxygen carried into the soil by the rainfall. Seasonal variations did not exceed 60 millivolts. Volk

did not think that E_h was a reliable indicator of the oxidation state of the soil, since it was dependent not only on the ratio of oxidized and reduced substances present, but also on the kinds and amounts of ions present. He also studied the effect of varying the E_h on the growth of plants (82). He was able to vary the E_h of the soil from 525 to 325 millivolts by the use of hydroquinone. There was no limiting effect of E_h on plants in the range of E_h studied. He concluded that E_h was not limiting to plant growth in Alabama soils.

In 1940, Keaton and Kardos (34), studied the effect of various materials on the arsenite-arsenate system. They found that ferric oxide raised the potential and caused arsenite to be oxidized to arsenate while clay shifted the equilibrium to the arsenite side. Alumina had no effect. They used the Nernst equation as a basis for their calculations. They concluded that ferric oxide in the soil caused increases in plant growth because of the oxidative effect on the arsenite-arsenate system which removed toxic arsenite by conversion to arsenate. They further concluded that the oxidative character of the soil was reflected in the redox potential and that the redox potential of the soil was the function of many complex interlocking systems. They therefore suggested that the redox potential was useful in the study and interpretation of the general chemical processes taking place in the soil.

In 1945, Starkey and Wight (77) made a very great contribution to the knowledge of redox processes in soils in a study for the American Gas Association. They studied the effect of soil conditions on the corrosion of iron gas lines buried in the soil.

The evidence which they obtained from various sources indicated that sulphate reducing bacteria were very important in anaerobic corrosion. The evidence indicated that the sulphate reducing bacteria were able to utilize energy from the oxidation of hydrogen, a redox reaction in which sulphate was reduced to sulphide. On the basis of E_h and pH measurements it was possible to predict severity of anaerobic corrosion of steel and cast iron in the soil. The reaction range for Sporovibrio desulfuricans in a culture medium was found to be 5.5 to 8.5. In soils, anaerobic corrosion was most severe at near neutral reactions. Soils more acid than pH 5.5 were considered unfavorable for anaerobic corrosion and no evidence of corrosion was noted in soils more acid than pH 5.5. The redox potentials of culture media of S. desulfuricans was initially 300 to 400 millivolts and dropped to 200 to 300 millivolts during growth of these sulphate reducing bacteria. Nearly as low potentials were observed in a sterile medium to which sulphide was added. The E_h of sterile media to which metallic iron was added became stabilized at 400 millivolts and this potential remained unchanged even after the growth of S. desulfuricans in the medium.

The E_h of rapidly decomposing plant residues was low even when the materials were kept moist and were presumed to be decomposing aerobically, but slowly decomposing plant materials had higher potentials. Similar plant residues decomposing under anaerobic conditions had low potentials. In moist soils containing organic matter, potentials remained high (above 400 millivolts) but similar soils in the waterlogged condition had low potentials (below 200 mv.). Subsoils, low in organic matter, showed scarcely any decrease in redox potential except when organic matter was added.

Acid extracts from aerobic and anaerobic soils showed little difference in redox potentials and little correlation with soil reductiveness. Potentiometric titrations however, showed wide differences between acid extracts from aerobic and anaerobic soils and even large quantitative differences between strongly reduced soils. These differences appeared to be due to chemical composition of the soils, in particular the iron content.

It was decided to use E_h and pH as a method of distinguishing corrosive soils and an instrument was devised for measuring the E_h of soils at depths of 3 feet or more. It was adapted only to wet soils. Electrodes were cleaned with an acid solution of a synthetic detergent and a solution of hydrogen peroxide. A scale of corrosiveness was set up based on soil redox potential. Each site was classified as to severity of corrosiveness on the basis of soil E_h and condition of the pipe.

The results of 48 test sites were tabulated. In 10% of the cases E_h failed to indicate the corrosive nature of the soil. In 67% of the cases the prediction was correct and in the remainder of the cases the degree of corrosiveness was predicted with only fair accuracy. In another test, results were less favorable where seasonal fluctuations in soil reductiveness occurred or where stray current electrolysis occurred.

Anaerobic corrosion was most severe in soils that had redox potentials between 0 and 100 mv. and was not observed in soils with redox potentials over 400 mv. Where water stagnated in poorly drained areas, anaerobic corrosion occurred. Where the soil water was in motion however, low redox potentials were not observed.

In 1943, Norman and Bartholomew (57) studied the composition of organic matter. They estimated the polyuronide content of soil organic matter by boiling in 12% hydrochloric acid and measuring the carbon dioxide produced. The "B" horizons of a number of Podzol soils were high in uronide content. Polyuronides occur in all plant materials and are also produced by microorganisms. Uronic acids (hydrolytic products of polyuronides) form soluble salts with monovalent cations and insoluble salts with divalent cations. They may act as agents of translocation in the Podzol weathering process.

In 1945, Starkey (75) reported on the types of bacteria which are active in oxidizing ferrous iron. Siderocapsa, Sphaerotilus, Clonothrix, Leptothrix, Crenothrix and Gallionella are all types of iron oxidizing organisms. Species of Gallionella are autotrophic and acquire energy strictly by oxidation of ferrous to ferric hydroxide, forming twisted ribbons or stalks of $Fe(OH)_3$. They are the most common type. They thrive at temperatures from 0°C to 22°C with an optimum at 6°C and are not sensitive to light. They like a range in iron concentration of 0.1 ppm to 30 ppm in a slightly acid reaction under aerobic conditions. They are most common on the surface of stagnant pools of water or near the roots of trees. Numerous heterotrophic organisms other than the above may decompose complexing organic anions, thus releasing complexed iron, which may or may not be precipitated, depending on conditions, pH, O_2, $Fe^{++} \rightleftharpoons Fe^{+++}$, concentration of Fe^{+++} ion, etc. Starkey performed a number of experiments and made several conclusions. In general, the principal effect of microbial activity was in the solution of iron. In precipitation experiments most of the iron was precipitated by strictly chemical means as a result of variations in oxygen and hydrogen content of the solutions.

In 1947, Matelski and Turk (44) studied the heavy minerals in some Podzol profiles of Michigan. The soils studied were Wallace, Kalkaska, Emmet, Rubicon, Roselawn, Grayling and Eastport sands. The heavy mineral suite was hornblende, garnet, epidote, zircon, tourmaline, tremolite, muscovite and opaque minerals. Magnetite made up 90% of the opaque minerals. Garnet was the most resistant to weathering of all heavy minerals. They showed that organic matter is an effective weathering agent in the formation of podzols. The "B" horizon showed a greater loss in heavy minerals due to weathering than the "A" horizon which in turn was more weathered than the "C". The "B" horizon also was more able to support vegetative growth than the "A" or "C".

In the same year Quispel (65), measured redox potentials _in situ_. He studied the soils in Holland that were inundated during World War II, and found potentials as low as -250 millivolts. He used platinized platinum electrodes and found the results more reproducible. Due to the great variance between measurements _in situ_, Quispel recommended that a great many readings be taken. He found that oxygen affected the redox potential greatly and thus the redox

potential was determined in part by the state of aeration of the soil. When the potential of the soil was determined in the field it was possible to define the aerobic or anaerobic character of the soil in terms of E_h.

In the same year Roberts (67) reported that *Bacillus polymyxa* in the presence of glucose, reduced ferric oxides or ferric hydroxide. The fermentation of glucose was more rapid in the presence of ferric hydroxide and the production of hydrogen was reduced. Roberts tested a number of cultures isolated from the soil and found that only *B. polymyxa* and one culture of *Clostriqium Spp.* reduced iron in considerable amounts. These were facultative aerobic bacilli.

Bertramson and White (4) give an excellent review of the literature dealing with oxidation and reduction in recent years. They concluded that the E_h of the soil represented the sum total of the oxidizing and reducing tendencies in the soil and depended on the nature of the system. The redox system varied with the nature of the soil and varied from soil to soil. They were critical of present laboratory techniques since there is no suitable method for measuring E_h in a manner similar to the measurement of pH. They suggest that the field quick test for ferrous iron may be more suitable for the measurement of reducing conditions in the soil.

In 1949, LaFonde (36) reported on the redox characteristics of several types of forest humus from Wisconsin and Quebec. He measured pH, redox potential and the total quantity of reduced substances by titration with permanganate solution. His results showed that mull humus was characterized by a positive redox potential and a strong acidity. He concluded that redox potentials could be used to characterize forest humus types.

In the same year Wilde et al (85) studied the electro-chemical properties of the ground water in the four major types of organic soils in Wisconsin. They measured pH, specific conductivity and redox potential in moss peat, wood peat, sedge peat and muck. The ground water underlying the four soils possessed specific electro-chemical properties. All results were highly significant. They concluded that electro-chemical analysis of ground water was important in dealing with problems in drainage of muck or peat soils and regulation of the water table.

In 1949, Joffe (33) gave a summary of the literature on Podzol formation. He described the genesis of a Podzol as that process which is initiated under the influence of a cool, humid climate with a vegetative cover usually of forest. It is controlled in a large measure by the plant food resources. The process is characterized by the rapid leaching of bases, development of an acid reaction, release of silica through mineral decomposition, and finally the removal of sesquioxides and their accumulation in the form of ortstein, orterde or concretions.

According to the literature, the "B" horizon may be soft and easily friable in which case it has been called "orterde". The "ortstein" has been differentiated into 3 forms. "Branderde" is a form of "B" horizon which is rich in organic matter but not cemented. "Ortstein" may be dark brown to black, hard as a rock containing organic matter or a dark brown ortstein which is very hard and contains only a very small amount of organic matter.

The iron and aluminum move as sols protected by organic substances and by silicic acid sols as well as by the cations Ca, Mg, K, Na, and the anions SO_4, PO_4, and CO_3. If the amount of organic matter present is small, iron ortstein low in organic matter forms. If there is a large amount of organic matter, iron-organic matter ortstein forms, poor in iron. Concretions should not be looked on as inherent to the podzolization process.

Limonite and gibbsite are the usual forms of iron and aluminum in the "B" horizon. They serve as cementing materials for ortstein and concretion formation. Manganese also tends to accumulate in the "B" horizon. Some concretions contain both manganese and iron. Phosphorous also tends to be fixed in the "B" horizon as phosphates of the sesquioxides. A polygorskite mineral (magnesium aluminum silicate) has also been identified.

The A_2 horizon (bleicherde) has been strongly leached. The removal of sesquioxides accounts for the white color. Most of the literature describes it as being the most acid horizon in the profile.

Joffe suggests that concretions have formed as a result of a change in the oxidation system in the soil.

In 1949, Deb (24) reported on the movement and precipitation of iron oxides in Podzols. He reviewed the mechanisms that have been suggested. The movement of iron as a positive iron oxide sol in association with alumina and humus cannot be established unless it is shown that the A horizons of Podzols are positively charged. This had not yet been established. It is not likely that iron oxide sols

could move as silica protected sols because the peptization of silica occurs in alkaline conditions and is probably not important in acid solution. The movement of iron as negatively charged iron oxide sols protected by humus is explored further by Deb. It is also proposed that iron may move in the form of complexes with large organic ions. Deb prepared a number of peat and muck extracts and studied the mutual coagulation and peptization of the extracts with ferric oxide sols, observing the relative concentrations, and the reaction. He also studied the adsorption of iron by soils from complex organic salts of iron and organic acid. Deb found that humus could peptize iron oxide sols under conditions found in Podzols and that any iron oxide formed as a result of weathering would probably be fully peptized by organic matter. He found that the amount of humus required to peptize iron oxide sols was not more than one third of the amount of iron oxide which is a much lower value than that which was suggested earlier.

He could find no evidence that the precipitation of iron from humus protected sols was affected by exchangeable calcium in B horizons of Podzols, or that the adsorption of iron by soils from complex salts of organic acids is influenced by the pH or the amounts of exchangeable bases present in the soil. He suggested a microbiological mechanism for the precipitation of iron.

In 1949, Bouyoucos (15) introduced the nylon blocks for measuring soil moisture. Nylon blocks are more resistant than plaster of paris blocks to decomposition under wet conditions. Both the nylon blocks and the plaster of paris blocks have very steep resistance-soil moisture curves in sandy soils because of the poor ability of sandy soils to maintain tension forces with water. The blocks could be used, however, in sandy soils to indicate conditions of dryness or extreme wetness.

E. W. Russel (68) discussed modern theories on the weathering processes involved in the development of Podzols. Little is known about the chemistry of the Podzol process. It has long been suspected that the movement of organic matter is connected in some way with the solution and transport of sesquioxides. The problem is to determine what constituents of the organic fraction are responsible. It has been shown that finely dispersed acid humus particles can mobilize hydrated ferric oxide and carry it down into the subsoil. It has been shown that from 3 to 10 times its own weight of hydrated ferric oxide can be carried down into the subsoil by acid humus under the conditions that prevail in the Podzol.

Another possibility is the formation of complex co-ordination compounds of polybasic carboxylic acids with iron. The presence of these materials has been assumed, not demonstrated, in the downward moving waters. It is possible that the mobilization of ferric oxide by humic acids takes place by some similar mechanism.

The second problem concerns the precipitation of the translocated materials in the B horizon. It seems most likely that not all the materials are deposited, but only a small portion, while the remainder are carried away in the ground waters. There are many analyses of ground water to support this reasoning. However some people claim complete precipitation. The principal theories at present assume that the primary cause of precipitation is the increased pH in the B horizon. Mobilized soil colloids are assumed to acquire a negative charge from humic or silicic acids. That is, colloidal ferric hydroxide or aluminum hydroxide becomes coated with humic acid and thereby acquires a negative charge. These particles are precipitated out in the B horizon when they come into a region of higher pH. In this case there could be no formation of co-ordination compounds with organic acids because such compounds would be soluble in less acid conditions than occur at the top of the B horizon.

An alternative theory postulates the precipitation of clay colloids in the B horizon during summer droughts. The mineral particles would then acquire a negative charge which could then adsorb the positively charged iron and aluminum co-ordination compounds moving downwards in the percolating waters. The organic acids would then be attacked by microorganisms thereby releasing the iron and aluminum hydroxides. The hydroxides, being positively charged would then adsorb silicic or humic acid. This theory approximates Mattson's theory for he has shown that the precipitates are isoelectric at the pH prevailing there.

Russel states that more factual information is necessary. In particular, information is needed about the forms of organic matter that actually move down through the A_2. The newer methods of organic matter analysis should give better knowledge of the components of organic matter particularly those that move from the A_0 into the B. There should also be more knowledge of the products of weathering that are not precipitated in the B horizon, but are carried away in the drainage water.

In 1950, Pierce (61) studied the prairie like mull of Downs silt loam, one of the most conspicuous forms of mull in the prairie forest region. Measurement of pH, specific conductance and redox potential indicated an intermediate position between Carrington silt loam and Miami silt loam which was taken to indicate that the soil was originally a prairie soil which had undergone a slight modification as a result of becoming forested.

In 1951, Bloomfield (5) studied the process of gleying. His results indicated that reduction of iron in the absence of oxygen may be partly due to the activities of microorganisms. His results are interpreted as evidence that degradation products of plants are in part responsible. He also discovered that ferric oxide was capable of fixing ferrous iron in solution. He compared the fixing properties of alpha, beta, and gamma varieties of ferric oxide using ferrous sulphate. He found that weight for weight the alpha form (goethite) had the greatest capacity for fixation and that a large portion of the ferrous iron was adsorbed. This occurred under aerobic conditions. Further experiments showed, that in the absence of air, ferric oxide had no effect but that, in the presence of air, the ferric oxide increased the degree of oxidation of ferrous iron markedly above that which occurred in an open ferrous sulphate solution. This suggests that ferric oxide in some way caused the ferrous iron to be less stable and made it more easily oxidized by oxygen in the air.

The above experiment also suggested a method whereby ferrous iron could be oxidized on being adsorbed by ferric iron in the B horizon of a podzol. The process is self renewing.

In 1952, Mackenzie (42) reported on studies of cold precipitated hydrated ferric oxide, which is found widely distributed in soils and soil clays, by means of differential thermal, X-ray, and electron diffraction methods. He suggested that these oxides may be precipitated from soil solution by ammonium hydroxide or some other similar ammoniacal material, or by hydrolysis of ferric salts in the soil solution.

The same year, Leeper (39) discussed the factors affecting availability of micronutrients in soils. The nature of primary minerals, exchangeable ions, simple precipitates with anions, oxidation-reduction processes, unavailable and available complexes (soluble), aging and recrystallization, and competition by microorganisms are some of the factors discussed. He suggests that iron and manganese are affected by the oxidation processes in the soil.

In 1952, Bloomfield (7) reported on further studies of the gley process in soils. He concluded that the iron content of mottled gley soils is essentially that of the ocherous mottles, the formation of which is a secondary effect of the gley process. In the gray portion of mottled gley soils, or in a peat gley, the process causes extensive mobilization of iron. Aluminum, in the mottled gley soil, followed the distribution of iron but in the gley soil it did not. This suggested a difference in the solubility of aluminum from that of iron in the gley process. He suggested that the gley horizons in a soil consisted in part at least of a sorption complex between ferrous organic compounds and the clay fraction.

In 1953, Bloomfield (6) reported on a study of the effect of aqueous extracts of Scots Pine needles on the iron and aluminum in the soil. He reported that an aqueous extract of the Scots Pine needles was capable of dissolving ferric and aluminum oxides and causing the iron to be reduced to the ferrous state. Solution and reduction took place under neutral and aerobic conditions. The ferrous iron was present in the form of organic complexes and possibly the aluminum also. The rate of oxidation of the ferrous complex was low but increased at higher pH's. At pH 7.0 the oxidation product was a soluble ferric complex and at pH 4.0 the products were precipitated. The soluble ferric complex remained in solution to a large extent and the ferrous complex remained in solution in relatively large amounts even at pH 8.0.

In 1953, Pierce (62) studied the pH, specific conductance, and redox potential of ground waters in Wisconsin. He found a close correlation between the redox potential, the oxygen content of the ground water, and with the rate of tree growth. The specific conductance influenced the forest type rather than the rate of growth. Later studies in Hearst, Ontario confirmed these results.

In the same year Bloomfield (8) reported a study on the mobilizing effect of Agathis Australis (Kauri) on the iron and aluminum in the soil profile. Results were similar to those for the Scots Pine.

In 1954, Lag and Einevoll (37) in studies on the water permeability of raw humus in podzol profiles, found that humus differed greatly in permeability from place to place. They had already shown a relationship between local microrelief and the thickness of the A_2 horizon of podzols. Under the surface depressions, the A_2 was noticeably thicker. They explained that this was due to the greater quantity of water percolating through the soil in the depressions. In view of this, the permeability of the humus on the surface would also affect the amount of water that could percolate through the soil.

In 1954, Bloomfield (9,10) also reported on further studies of reduction and solution of ferric iron and mobilization of aluminum by various leaf extracts. He used Rimu (Dacrydium cupressinum), a New Zealand species, Norway spruce, Sitka spruce, Douglas fir, and Larch, which is a deciduous conifer. All gave similar results. The iron oxides dissolved with the formation of organic complexes, the ferric iron undergoing reduction even in the presence of oxygen. Further studies with leaf extracts from ash and aspen (11) also reacted with ferric and aluminum oxides to form soluble metal complexes, and the ferric iron was reduced to ferrous iron under aerobic conditions. In contrast to the conifers, the aspen continued its ability to carry out the process at high pH values. Bloomfield also suggested that since aspen and ash leaves contain relatively large quantities of water soluble calcium, they may account for the high base saturation status of Grey-Wooded soils.

In a subsequent paper in the same year, Bloomfield (12) studied the precipitation of the mobilized sesquioxide complexes. Solution of the oxide reaches a maximum and subsequently declines with the formation of coatings of adsorbed ferrous iron complex on the ferric oxide particles. Leaching through sand columns produced similar coatings on the sand particles. In other words, iron and aluminum leaf leachate compounds or complexes were adsorbed on soil colloids. The sorption was found to vary inversely as the efficiency of the species as a mobilizing agent.

In 1954, Bloomfield and Gasser (13) studied the mobilization of phosphate in waterlogged soils. The effect of anaerobically fermenting plant material on the mobilization of aluminum, calcium and iron phosphates was studied. The aluminum phosphate could not be mobilized. Calcium and iron phosphate could both be mobilized. Basic ferric phosphate readsorbed phosphate. Kaolin and montmorillonite fixed phosphate from fermenting grass solution. Phosphated clays released about half of the phosphate which had been "fixed" on the clays to the fermenting grass solution. With montmorillonite the amount remaining fixed by the clays was equal to the amount removed from fermenting grass solution by untreated montmorillonite.

Oxidation of fermentation solutions containing iron and phosphate gave a precipitate of basic ferric phosphate together with organic matter. They suggested that since this is a relatively stable precipitate it accounts for the movement of phosphate in association with iron within the soil profile.

In the same year McKenzie and Erickson (49) reported on the use of redox potentials in studies of soil genesis. Redox potentials in soil profiles and in sand columns gave evidence that there was a redox profile in the soil. Further studies were warranted.

In 1954, Bromfield (90) studied iron reducing organisms. He made isolations from a soil treated with sugar and artificially gleyed, from a gleyed soil, and from fermenting grass. Organisms from the genera *Escherichia*, *Aerobacter* *Bacillus* and *Paracolobactrum* were identified. All produced ferrous iron in ferric hydroxide media.

The most active organisms, *Bacillus polymyxa* and *Bacillus circulans*, were isolated for further study. Under anaerobic conditions these organisms reduced iron. Under aerobic conditions they also carried on reduction, but the amount of ferrous iron produced varied as the surface area of the media used. Under anaerobic conditions the organisms were unable to utilize the oxygen from ferric oxide for growth, but in the presence of another oxygen bearing compound capable of being utilized, reduction of ferric oxide and growth occurred. Ferric iron reducing organisms were present in the surface layers of gleyed soils but were not present at depths of 10 feet.

In 1955, Sowden (74) reported results of studies on estimation of amino acids in soil hydrolysates using the Moore and Stein method. He found no distinctive difference in the amino acid distribution of three soil types. The percentage of amino-N was higher than expected.

In 1955, Flaig, Scharrer, and Judel (25), in Germany, reported investigations on the determination of redox potentials in soils. They found that reproducible redox potentials could only be obtained in aqueous solutions, and aqueous soil suspensions, when the dissolved oxygen in solution is displaced by an absolutely pure inert gas like nitrogen. The reproducibility and the velocity at which the redox potential is established depends mainly on the effect of the previous handling of the electrodes. Form and size of the electrodes and the electrode vessels showed no special influence on the redox potential. Likewise the error which arises through the neglect of the temperature falls within the error limit of the method. The establishment of potentials by the platinum electrode is an equilibrium reaction between the redox system and the electrode. Through agitation and more intense introduction of nitrogen, the diffusion within the solution being measured is improved and the establishment of the potential accelerated. In the case of all cited investigations a saturated calomel immersion electrode was used as the reference electrode. A potassium chloride diffusion from the electrode into the measuring solution was maintained by a suitable construction of the potassium chloride bridge. The previous history of the platinum electrode is very important in the reproducibility and the equilibrium adjustment of the potential. The connection between the previous handling and the effect on the redox systems was discussed and examples cited. The redox potential was higher, the greater the proportion of solid particles in the soil suspension. A definite soil-water ratio should always be maintained. The length of time, during which the suspension was agitated, in

order to disperse the soil particles and to bring the water soluble parts into solution was, within certain limits ($\frac{1}{4}$ up to 2 hrs.), without noticeable influence on the redox potential. In the case of transferring the suspension to be measured from the sintered container for agitation to the electrode container, care was required that no sedimentation occurred. A continuous measurement of pH with a glass electrode during the redox determination was not feasible because of the suspension effect and the colloid adsorption. On a similar basis a glass electrode could not be used as the reference electrode for the redox measurement. It was shown that the redox determination of air dry soil samples was of little value since they were slowly oxidized in the air. In order for the redox potential of the undisturbed soils to be obtained, the samples should be suspended and measured in the fresh unaltered state.

In a second paper (26) the authors discussed the results of redox measurements and titrations from a study of a number of soils.

In 1955 (69) Schnitzer and De Long studied the ability of leaf extracts to mobilize and transport iron. The material present in extracts of Populus grandidentata (poplar) was an acidic polysaccharide. There was no evidence of chelation.

In 1956 Schnitzer and Wright (70) reported on the results of leaching a column of calcareous sand with ethylenedeaminetetraacetic acid (EDTA) which is a strong chelating agent. Sesquioxides were deposited in the B horizon in the column.

SUMMARY OF LITERATURE

A. Theories of Podzol Development

The Podzol profile is characterized by an ashy A_2 horizon which is strongly leached and is often the most acid part of the profile (33). The A_2 horizon changes abruptly into a sharply contrasting brown to dark reddish brown B horizon which contains an accumulation of sesquioxides and organic matter. Phosphate also tends to accumulate in the podzol B horizon (33). The B horizon changes gradually into the underlying light yellowish brown C horizon forming a diffuse boundary between the B and C horizons which is difficult to define. In some cases, the B horizon may be subdivided into two parts, the upper B_{hir} horizon which is very dark reddish brown and is the zone of maximum organic matter accumulation and the B_{ir} horizon which is brown or reddish brown.

Figure 1. Photograph of a strongly developed Podzol Profile, Wallace sand.

Overlying the ashy A_2 horizon is a group of thin horizons, the

A_{oo} which is composed of relatively fresh plant remains, the A_o horizon which is composed of decomposed plant materials, and the A_1 horizon which is a mixture of decayed plant remains, humus and soil particles. The A_1 horizon may be absent (58). In any case there is an abrupt change from the A_o or A_1 into the bleached A_2 horizon.

The sharp boundary between the A_2 horizon and the B_{hir} horizon and the diffuse lower B_{ir} suggest a more or less complete precipitation of mobile materials which are largely organic, or a complete mobilization of the sesquioxides in the A_2 horizon and translocation of the mobilized materials into regions lower in the B where a gradual immobilization occurs. This suggests that the process is the result of the downward movement of percolating waters and that some or all of the mobilized materials are removed from the percolating waters by some mechanism such as adsorption or precipitation. Such a thesis would not suggest that the percolating waters dissolve soil constituents from the A horizon, move downward into the B horizon and remain there until a drying process occurs during the summer to deposit and fix the soluble materials as Dr. Albert suggested (1, 2) but that the percolating waters move completely through the profile and the soluble or mobilized colloidal materials are removed by some definite process or agency. The tongued nature of the B horizon indicates the channels where most of the percolating water travels through the soil into the underground regions where it joins the ground water supply. Dr. Albert in Germany (1, 2) has shown that there is a relation between the

depth of penetration of summer rains and the depth of the B horizon of the Podzol below the surface. It is not intended that this thesis refute his work, but we must also account for those periods in the year when the water in the upper soil horizons is connected with the ground water supply. Under these conditions the addition of surplus water to the surface horizons would lead to a transfer of the excess water in the soil to the ground water supply. Such a condition exists in the northern part of the lower peninsula of Michigan during the winter and early spring months. During that period, the soil, under a good snow cover, does not freeze but is cool and moist all winter long. Such conditions are suitable for solution of materials in the upper layers of the soil and for almost continuous movement of water downwards to the ground water, laden with mobilized soil constituents.

The sharpness of the A_1 - A_2 boundary suggests a more or less complete conversion of certain parts of the plant materials into mobile or water soluble constituents which are carried beyond a definite boundary, while the residue is quite immobile and remains behind in the A_1 in the form of humus. This form of reasoning leads to the assumption that the water soluble, mobile constituents of the organic matter together with the products of the metabolic activities of the microorganisms in the surface horizons, are the mobilizing agents for other constituents. The evidence in the literature substantiates these observations (5, 6, 7, 8, 9, 10, 11, 13, 75). It has been established by Bloomfield (5, 6, 7, 8, 9, 10, 11, 13) that fresh organic materials have the power to reduce ferric oxide to ferrous oxide and thereby mobilize iron in the A horizon. He has also shown that the organic materials form complexes with iron which are mobile or soluble and can move downwards in the soil. In general, then the function of the organic matter in the podzolization process is the mobilization of sesquioxides, in the A horizon.

It is also known that a shallow Podzol with a thin A_2 horizon can form in 20-25 years (68). This suggests that the process begins near the surface and the early thin A_2 gradually thickens downwards through remobilization of precipitated materials in the B horizon until an equilibrium with the environment is attained and the soil has reached the stage of development which is recognized by pedologists as the mature soil. Visible Podzols also tend to form more quickly and to be more strongly developed on sandy soils than on finer textured soils. Possible reasons for this are the relatively lower total surface areas of sandy soils, their high permeability and their higher aeration status.

Once the sesquioxides, organic matter and silicates are mobilized they are translocated to regions lower in the profile and precipitated there. Several possible methods of precipitation have been presented in literature. Mattson's theory of isoelectric precipitates (45, 46, 47) suggests a reasonable possibility which can occur under the conditions of acidity prevailing normally in soils. Silica and humus are electronegative while sesquioxides are electrical ampholytes being electropositive in acid solution and electronegative in alkaline solution. The position of the isoelectric point relative to pH depends on the nature of the combining anion which is present when the sesquioxides are in the electropositive state. Oxides of aluminum and iron can form precipitates with silicates, humus and phosphoric acid under conditions commonly found in soils. Oxidation of adsorbed materials during periods of summer dryness may also play a part. It seems likely that translocation of dissolved sesquioxides in true solution must also play an important part (49). However it must be shown that conditions for oxidizing ferrous iron in true solution do exist in the regions of the B horizon. The presence of adequate amounts of oxygen or some other material oxidizing ferrous iron in the region of the B horizon would supply the required conditions. Iron oxidizing bacteria could also perform such a function.

The genesis of the Podzol profile seems therefore to be the result of mobilization of sesquioxides and organic matter possibly through the activities of microorganisms in part and also through the process of iron-organic complex formation and the translocation of these materials in solution or suspension to regions lower in the soil where they are precipitated. The means of precipitation suggested are precipitation of colloids in a region where soil reaction conditions are isoelectric for the colloids, precipitation by drying and resultant oxidation, precipitation from solution by means of oxygen or some oxidizing agent other than oxygen, or precipitation by means of microorganisms capable of oxidizing iron itself or organic complexes (75, 76) of iron.

B. Oxidation-reduction Potentials

Any anion or cation in equilibrium with its counterpart in a different state of oxidation is a redox system. It should be explained that the word redox is a contraction of the words oxidation-reduction for purposes of convenience and has been widely adopted in the literature. An example of such a system is the $Fe^{+2} = Fe^{+3} + (e^-)$ couple. Fe^{+2} and Fe^{+3} are the ions involved in the system; (e^-) is the electron change (the valence change in the reaction) undergone by the reactants. The E.M.F. of the electrode or couple cannot be measured unless it is compared with a standard electrode whose potential is known. The potential is a measure of the tendency of the electrode to donate electrons and thereby to be oxidized, or to accept electrons and thereby to be reduced. The hydrogen electrode ($H_2 \rightleftharpoons 2H^+ + 2e^-$), where the pressure of H_2 is 1 atmosphere and the H^+ ion is 1 molal in solution, has been chosen as the standard and its potential has been set at zero. Thus, when some other electrode or couple is compared with the hydrogen electrode, the potential observed is the potential of the unknown electrode. Many other electrodes have been compared with the hydrogen electrode and their potentials have been tabulated. Latimer (38) has prepared one of the most complete tabulations available. When two such electrodes are compared, the resulting system is known as a cell and each electrode is called a half-cell. When one half-cell is a system of ions in solution, contact is made by means of an inert noble metal which acquires the charge of the half-cell. Platinum is preferred as the connector and may be either shiny or platinized. When two such electrodes are connected, a current will tend to flow from one electrode to the other. The potential measured across the electrodes is known as the E_h of the cell when it is compared with the standard hydrogen electrode. When another standard cell is used a correction must be made to refer back to the hydrogen electrode. The saturated calomel electrode is such a standard and is widely used since it is portable. In the convention used by Latimer (38) the potential of the saturated calomel electrode is -.245 volts and must be applied algebraically to the measured emf to compare with the standard hydrogen electrode. The saturated calomel electrode has been used in this work and the potentials given for the soils studied are compared to the saturated calomel electrode. (Fig. 4, 5, 6 and appendix.)

The potential of a cell may be calculated by use of an equation developed from the Nernst equation -

$$E_h = E_o - \frac{RT}{nF} \text{Ln} \frac{(OX)}{(Red)} \qquad (1)$$

where E_h is the emf of the cell, E_o is the standard potential of the electrode being compared with the standard electrode, R is the gas constant, T is the absolute temperature, n is the number of electrons involved in the reaction, F is the Faraday (96,500 coulombs), (OX) is the activity of the oxidant and (Red) is the activity of the reductant. When at 25° (298° absolute) and converting from natural logs to the base 10., the equation simplifies to -

$$E_h = E_o - \frac{.059}{n} \text{ Log } \frac{(OX)}{(Red)} \qquad (2)$$

In the case of very dilute solutions it may be assumed that all activities are equal to 1 and the actual concentrations may be used. When the activities of the oxidant and reductant are equal, it can be seen that -

$$\frac{.059}{n} \text{ Log } \frac{(OX)}{(Red)} = 0$$

and therefore $E_h = E_o$.

This means that when the reactants in the cell are 50% oxidized and 50% reduced the E_o of the cell is a standard value which can be compared with other systems. All known systems can therefore be arranged in a scale in order of their E_o values. The E_o value of an electrode is a measure of its ability to donate or accept electrons, it is a measure of the tendency of a one system to oxidize or reduce another. In Latimer's convention those systems with high negative E_o values are strong oxidizing agents and those with high positive values are strong reducing agents. When the two electrodes are coupled, the emf. measured is the algebraic difference of the E_h's of the two electrodes. The magnitude of the E_h then is a measure of the rate at which the reaction will proceed. Those electrodes with high or low E_o values are widely used by chemists in redox reactions. In some cases catalysts can be used to accelerate the reactions.

In the literature it has been reported (17, 19, 20, 22, 27, 30, 35, 49, 51, 56, 62, 65, 77) that organic matter, humus, clay minerals, iron, manganese, oxygen and sulphur are some of the substances that take part in redox reactions and which may determine the redox potentials observed in the soil. Each substance is present in the soil in the form of a redox couple, that is, both an oxidized and reduced form of each substance will be present in varying amounts depending on the oxidation state of the couple. The oxidation state of the couple depends on the nature of the other redox systems present in the soil at the same time. Keaton and Kardos (34) regard the soil system as a composite of complex interlocking redox systems. If the oxidation state of one redox system is changed, due to the effect of microorganisms or removal of oxygen or some other determining factor, all the other systems change until equilibrium is again reached. The redox system of the soil should then be regarded as a dynamic system affected by climate, topography and microorganisms which is continually changing, never at equilibrium, but always trying to reach equilibrium. The change is reflected in the change in E_h.

The redox potential of the soil is also affected by the hydrogen ion concentration. It increases directly as the hydrogen ion concentration increases. That is, the E_h-pH relationship is an inverse relationship. It was first reported by Willis (87) as being about .060 volts per pH unit, but later investigators (17, 59) have shown that it may vary for each soil or for each soil horizon. Using the Nernst equation it can be calculated for a particular redox reaction.

Some redox systems are more resistant to E_h changes than others.

The resistance of a redox system to change in E_h is known as the poise of the system. The poise of a redox system is similar to the buffer capacity of soils. Every system will undergo a change in E_h as the ratio of oxidant to reductant changes. The E_h curve is relatively flat where the ratio of oxidant to reductant is approximately equal to 1.0 but becomes very steep when the ratio of oxidant to reductant is extremely large or small. According to Clark et al (21), the system is well poised when the curve is flat, and the system is poorly poised when the curve is steep.

In soil genesis it is considered that there are five factors of soil formation (32). The action of microorganisms and organic matter on the soil particles, conditioned by the effect of climate and drainage operating for a period of time, results in the morphological expression of a soil profile which is at equilibrium with the environment when at maturity. When the redox potential is measured in the soil <u>in situ</u>, the effect of climate, microorganisms and organic matter (vegetation), and drainage (topography) on certain mineral constituents of the parent material is expressed in the E_h. If the redox potential is followed over a period of time, all the soil formation factors are considered and the E_h of the soil is in part a measure of soil formation. There should therefore be a redox profile in the soil. Since the podzolization process, described above, is concerned with sesquioxides and organic matter which are complex redox systems, the study of the redox potentials of a Podzol profile is of interest, and may serve to indicate which of the theories are likely to be most important in the profile development.

Previous studies of redox potentials of soils in situ (35, 49, 65) have indicated that there is a large experimental error. If enough replicates are used, it should be possible to determine if the variance is due to experimental error or to the natural variance of the oxidation-reduction processes in the soil. It was therefore decided to use as many replicates as possible.

The effect of microorganisms is considered important as a part of the biotic or vegetation factor of soil formation. It was therefore decided to devise a method whereby those organisms oxidizing both organic matter and iron could be studied.

In the discussion and interpretation of the redox potential data a number of conventions are discussed. Those used by Peters (60) have been adopted in this thesis.

RESULTS

Soils Studied

For the study of redox potentials in situ it was decided to measure redox potentials by horizons (depth); and observe the changes in redox potential as they occurred with the seasons and with drainage. For this purpose, three soils were selected in one area forming a hydrosequence of soils developed on the same kind of parent material. They differed in drainage and although all three sites were under forest vegetation, the species on each site differed from the others.

Figure 2 below shows the relationship of the soils in the hydrosequence. Profile descriptions of the soils at each site are given below. The soils selected for study were the well drained

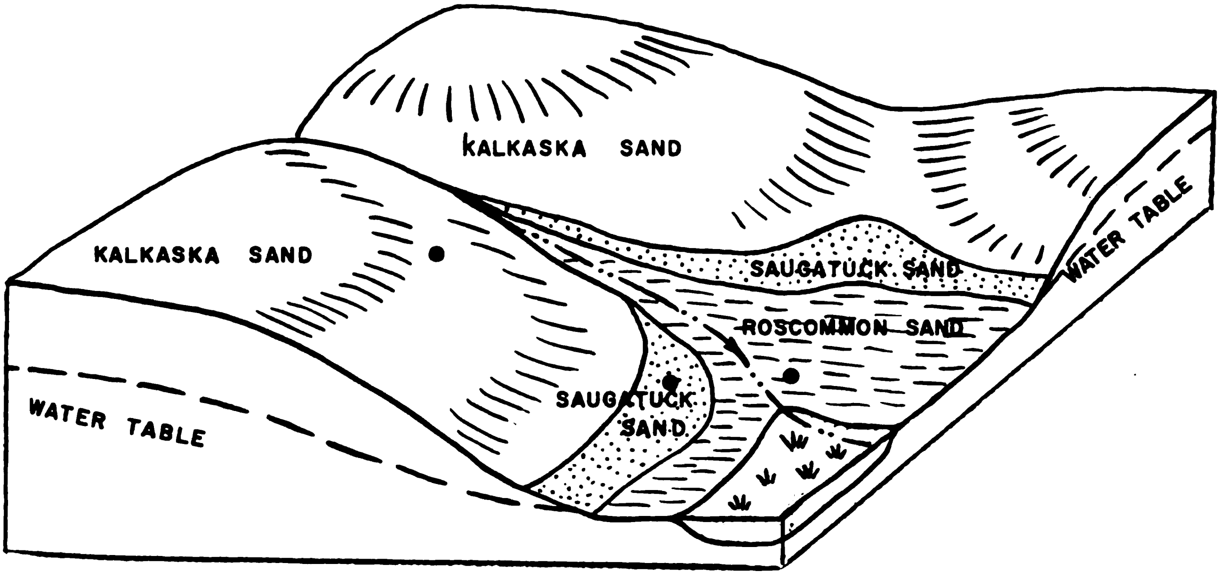

Figure 2. Diagram of Experimental Site Showing Relationship of the Soil Series.

Kalkaska sand, the imperfectly drained Saugatuck sand, and the poorly drained Roscommon sand. They form a hydrosequence of soils on the slope. The Kalkaska series is a well drained sandy podzol with a moderately developed B horizon. It was located at the top of the slope (Fig. 2). Where the series intergrades to the Wallace series it may contain some "ortstein" concretions (Fig. 1). The Saugatuck series is an imperfectly drained Podzol with a strongly developed "ortstein." It was located near the foot of the slope in the region of the fluctuating water table. The Roscommon series is the poorly drained sandy associate of the soils of the Podzol region of Michigan. The site was located at the foot of the slope, approximately 50 ft. North of the Saugatuck site, adjacent to a muck soil. The Roscommon series is slightly acid in reaction. The parent material of all three soils in the hydrosequence is sandy outwash or till which is extensive in the northern lower peninsula of Michigan.

Location and Physiography: The soils selected for study are located in the region of the Podzol Great Soil Group in the northern part of the lower peninsula of Michigan. The area is located in the hilly interlobate morainic area in the northwestern part of Osceola County. Elevations range from 1000 ft. to 1600 ft. above sea level, and the drift ranges in thickness from 800 ft. to 1200 ft. It is of late Cary age. A wide variety of textures and slopes occur. The site where the study was carried out was on an 8-12% slope, located in T 20 N - R 10 W (Burdell Twp.) section 10, NE¼, S. E. corner, 50 yds. west of the road.

Climate: The climate of the area is cool and humid (31, 84). The annual precipitation is approximately 30 inches. The winters are of particular interest. The snow cover reaches 1 - 2 ft. in thickness, and protects the soil from freezing, as well as supplying enough meltwater to keep it moist. During the time the study was being carried on the soil was never frozen. The last frost in the spring occurs from May 20 - 31, and the first frost in the fall occurs from September 10 - 20 (31). The growing season is 110 - 140 days long. The summer temperatures reach the low 90's. The summer season may be dry. The rainfall is of the thundershower type.

Vegetation: The vegetation consisted of sugar maple (Acer saccharum), aspen (Populus tremuloides), with bracken (Pteris aquilina), blackberries and wintergreen on the well drained and imperfectly drained sites and with hemlock (Tsuga canadensis), white cedar (Thuja occidentalis) and scattered alders on the poorly drained site. Profile descriptions of the series are presented below.

Kalkaska sand: The Kalkaska sand is the well drained member of the hydrosequence, developed on the brow of a 10% slope under the crown of a large sugar maple. There was no sign of erosion although later treatment of the surface horizon indicated the presence of charcoal, suggesting that the area had been subject to fire in the past.

Kalkaska Soil Profile

Horizon	Depth	Description
A_{00}, A_0	1½-0"	Dark grayish yellowish brown* (10 YR 2/1); mat of organic matter with a thin (½ inch) covering of fresh leaf litter; 1½ inches thick.
A_1	0-2"	Brownish grey (10 YR 4/1); sand; crumb structure; very friable; pH 5.2; 2 inches thick.
A_2	2-17"	Yellowish grey (10 YR 7/2); sand: loose; pH 5.1; 15" thick.
B_{hir}	17-23"	Dark grayish brown (5 YR 2/1 - 2/2); sand; coated with organic matter; strongly cemented in places, but soft and friable in others; pH 5.6; 6 inches thick.
B_{ir}	23-34"	Moderate brown (7.5 YR 4/4); sand; weakly cemented with scattered ortstein concretions; firm; pH 5.3; 11 inches thick.
C	34"	Light yellowish brown (10 YR 7/3); sand; loose; pH 5.5.

<u>Saugatuck sand</u>: The Saugatuck sand is the imperfectly drained member of the hydrosequence, developed at the foot of the slope, a few feet in elevation above the Roscommon site. The site was located six feet south of the trunk of a large aspen and under the edge of its crown. Apparently because of the effect of a strongly developed ortstein in the B horizon, and the presence of the high water table, the roots were mostly concentrated in the A_1 horizon with a few in the B_{hir} horizon.

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*I.S.C.C.-N.B.S. color names as given in National Bureau of Standard Circular 553, 1955.

Saugatuck Soil Profile

Horizon	Depth	Description
A_{oo}, A_o	1½-0"	Dark grayish brown (5 YR 2/1); organic layer with a ½ inch cover of fresh leaf litter; 1½ inches thick.
A_1	0-5"	Grayish yellowish brown (10 YR 5/2); sand; weakly coherent; very friable; medium crumb structure; with much organic matter; pH 4.8; 5 inches thick.
A_2	5-18"	Brownish pink (7.5 YR 7/2); sand, loose, very friable; pH 4.6; 13 inches thick.
B_{hir}	18-22"	Dark grayish brown (5 YR 2/1); sand; weakly cemented with organic matter; firm; pH 6.1; 4 inches thick.
B_{ir}	22-37"	Moderate brown (7.5 YR 4/4); mottled light brown (7.5 YR 6/4); sand; strongly cemented; pH 6.1; 15 inches thick.
C	37"	Light yellowish brown (10 YR 6/3); sand; loose; moist; pH 6.5.

Roscommon sand: The Roscommon sand is the poorly drained member of the hydrosequence. It was located in the bottom of a drainage way, at the foot of the slope in a clear space between alders and hemlock. The site was usually saturated with moisture in the late winter and spring. The water table was not normally much below the soil surface until early July.

Roscommon Soil Profile

Horizon	Depth	Description
A_{oo}, A_o	2-0"	Dark grayish yellowish brown (10 YR 2/1); moderately decomposed organic material with a ½ inch covering of fresh plant residues; 2 inches thick.

Roscommon Soil Profile (Cont.)

Horizon	Depth	Description
A_1	0-10"	Brownish grey (10 YR 3/1); fine sand; very friable, medium crumb structure; pH 5.4; 10 inches thick.
GA_{-1}	10-16"	Light grayish brown (7.5 YR 6/2); sand; loose; very friable; pH 5.9; 6 inches thick.
GB_{-1}	16-18"	Dark grayish yellowish brown (10 YR 3/2) mottled with 10YR 5/6 and 4/1; gravelly loamy sand; loose; pH 6.7; 2-4 inches thick.
GA_{-2}	18-31"	Light grayish yellowish brown (10 YR 6/3); sand; loose; pH 6.7; 13 inches thick.
GB_{-2}	31-32"	Grayish brown (7.5 YR 4/2) and very dark grayish yellowish brown (10 YR 3/2); sand; cemented; pH 6.7; 1 inch thick.
C_1	32-34	Light grayish brown (7.5 YR 5/2); fine sand; loose; pH 6.7; 2 inches thick.
C_2	34"	Light grayish yellowish brown (10 YR 6/2); sand; loose; pH 6.7.

Oxidation-reduction Studies

Electrodes were prepared as described by Quispel (65) and McKenzie and Erickson (49). In order to make them more sturdy, the glass tubing containing the wire leads was filled with castolite resin which was allowed to harden slowly after heating to 60°C for a short time. Treated in this manner, the castolite formed a flexible rod which was less subject to damage during installation. It was not necessary to remove the glass tubing. The electrodes were then cleaned, platinized, and tested for reproducibility. Only those electrodes checking within 2 to 3 millivolts were used. The testing solution was a solution of quinhydrone in .05 molar potassium-acid phthalate buffer which gave a pH of about 4.0. The quinhydrone dissociates in equal amounts of oxidant and reductant and therefore the E_h of the solution is constant. It thus serves as a good testing solution for standardizing electrodes. The electrodes were installed in the soils using the method described by McKenzie and Erickson (49). After installation, the tops of the electrodes were clipped off at the level of the A horizon and extensions of Belding 22 gauge insulated copper wire were soldered to the electrode leads. The connections were waterproofed with tygon paint. The extensions were connected to an instrument board mounted on a 3½ foot post. The installation permitted the measurement of the

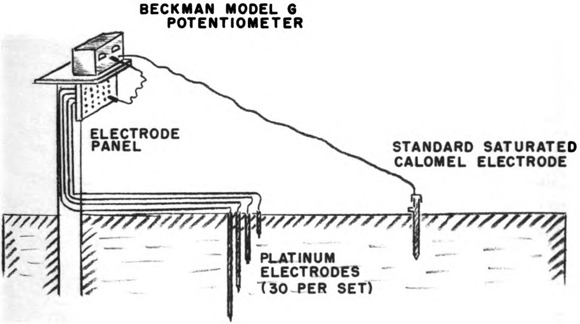


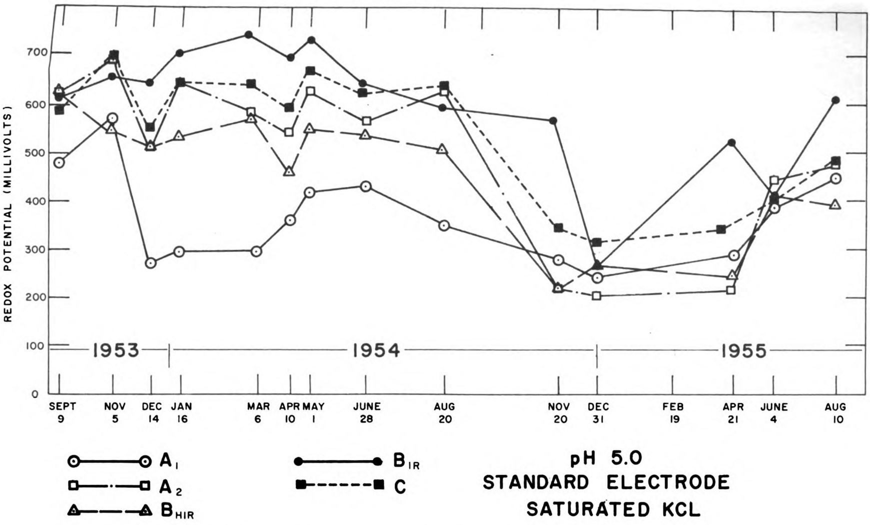
Figure 3. Diagram of Electrode Installation.

redox potentials during the winter, without disturbing the electrodes, unhampered by the depth of snow. Connection with the saturated calomel electrode was carried out by setting the calomel electrode in a hole prepared in the soil near the site. The soil was first moistened with a saturated solution of technical grade KCL. Potentials were measured using the Beckman model G potentiomenter. Figure 3 is a diagram of the installation. The electrode sets were protected with a wire guard. A wooden cover was installed over the wire leads at the electrode panel to protect them from the weather.

At each site, thirty electrodes were installed, six electrodes in each of five horizons. Measurements were made periodically over a period of two years. At the end of the experiment the soils were sampled, the electrodes were removed, examined, and the exact location of each electrode in the soil profile was determined. An E_h-pH measurement was run on each of the soil horizons using a variation of the method of Willis (87) with a nitrogen atmosphere. Results are recorded in the appendix. The correction was applied to the redox potentials of the soil to standardize them at pH 5.0. This experiment must be run on fresh soil samples since air drying results in oxidation of some of the soil constituents and may thereby alter the potentials. Results of these experiments are shown plotted in Figures 4, 5, and 6.

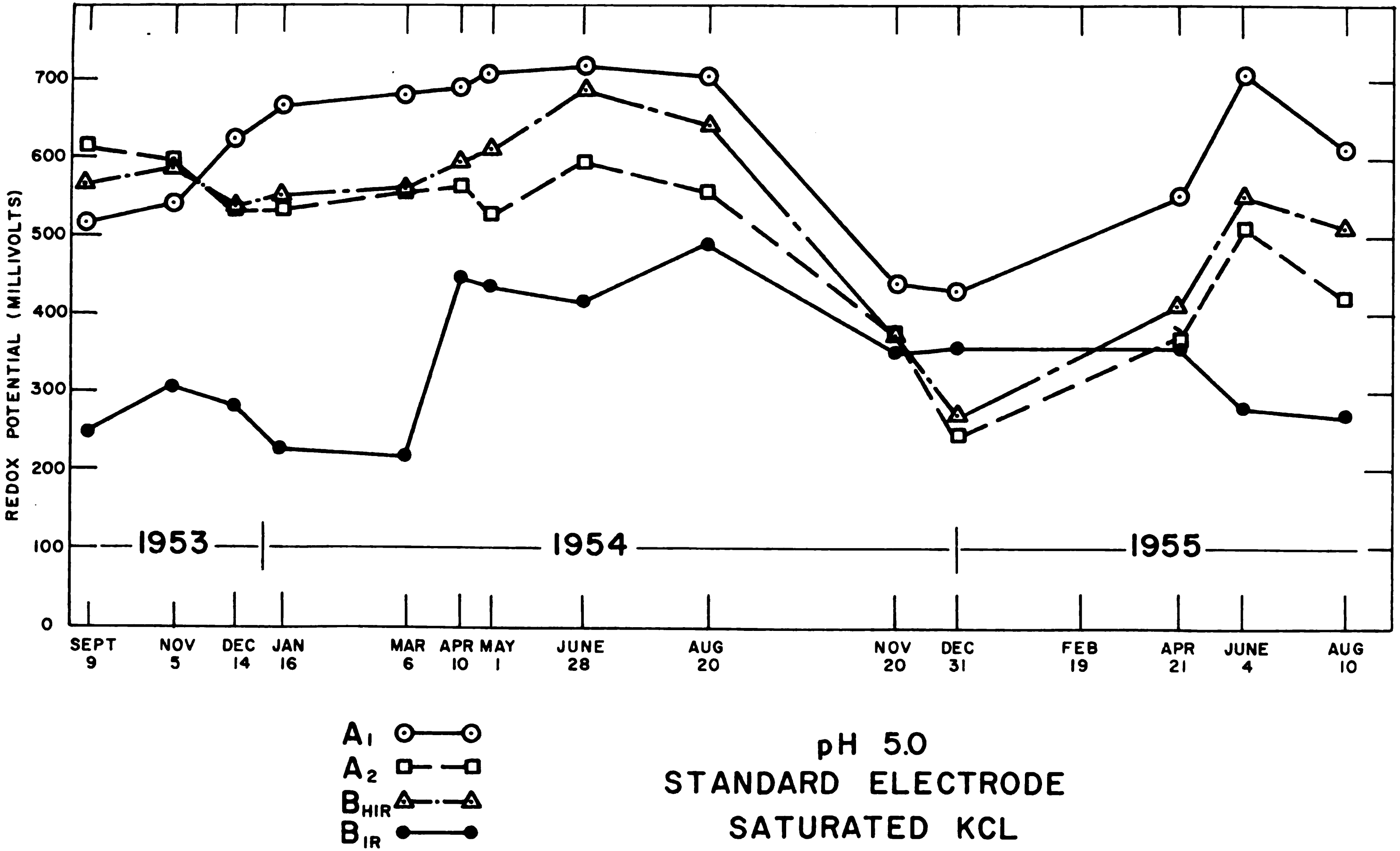
Physical and Chemical Studies

Mechanical analyses by the pipette method and mineralogical analyses were run on all three soils. For the minerological



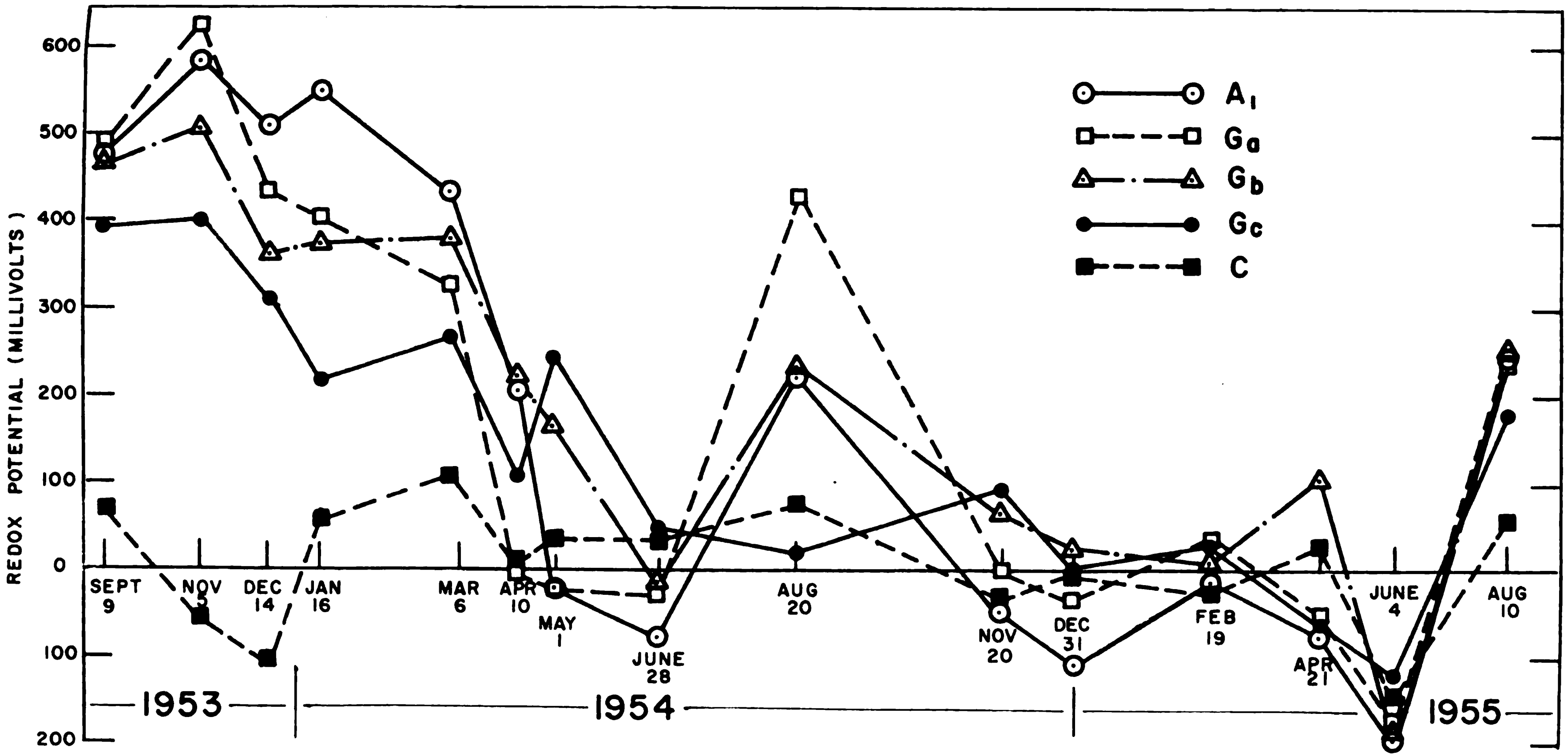
pH 5.0
STANDARD ELECTRODE
SATURATED KCL

FIGURE 4: SEASONAL VARIATIONS IN REDOX POTENTIAL FOR 5 HORIZONS OF KALKASKA SAND



pH 5.0
STANDARD ELECTRODE
SATURATED KCL

FIGURE 5: SEASONAL VARIATION IN REDOX POTENTIAL FOR 4 HORIZONS OF SAUGATUCK SAND



pH = 5.0
STANDARD ELECTRODE
SATURATED KCL

FIGURE 6: SEASONAL VARIATION IN REDOX POTENTIAL FOR 5 HORIZONS OF ROSCOMMON SAND

analyses, the fine sand fractions were used. The heavy minerals were separated using s-tetrabromoethane adjusted to S.G. 2.85 with nitrobenzene. An additional check of the light mineral fraction was obtained by x-ray analyses using the Norelco x-ray spectrometer. In addition, volume weight, solution loss, total carbon by the hydrogen peroxide method, permeability, porosity, the base exchange capacity of the mineral fraction were run on the Kalkaska sand profile. The results of the mechanical analyses are given in Table 9 in the Appendix and are shown in cumulative percent composition curves in Figures 7, 8, 9. The values of sorting, kurtosis and skewness were calculated for the horizons of the three soils. Results (Table 12 in Appendix) indicate stratification in the Roscommon and Saugatuck series. There is some variation in the Kalkaska series also.

Microbiological Studies

In order to further characterize the soils, it was decided to study the distribution of microorganisms in the profiles of both the Saugatuck and Kalkaska series. Iron complex forming organic anions may be important in the podzol process (5, 6, 7, 8, 9, 10, 11, 14), and may determine soil redox potentials in part (51, 72, 73). There are microorganisms which can utilize such anions as a source of energy (55, 77). They may also contribute to the redox potential of the soil (27). Citrate is such an anion. When ferric citrate agar medium is used, the colonies of organisms are stained a reddish brown color and can be counted. Therefore, ferric citrate agar medium was selected to test for the presence of complex forming organic anions

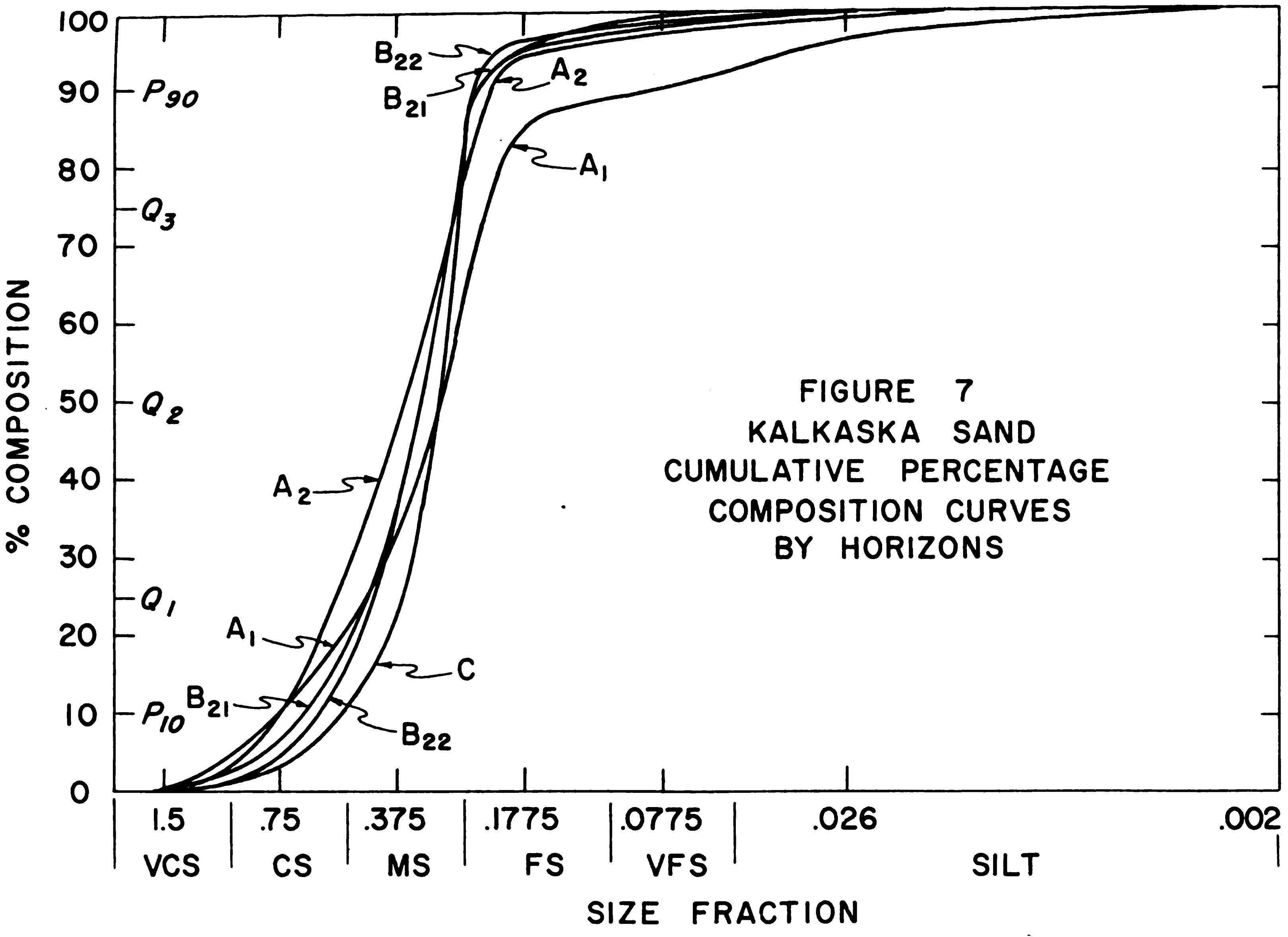


FIGURE 7
KALKASKA SAND
CUMULATIVE PERCENTAGE
COMPOSITION CURVES
BY HORIZONS

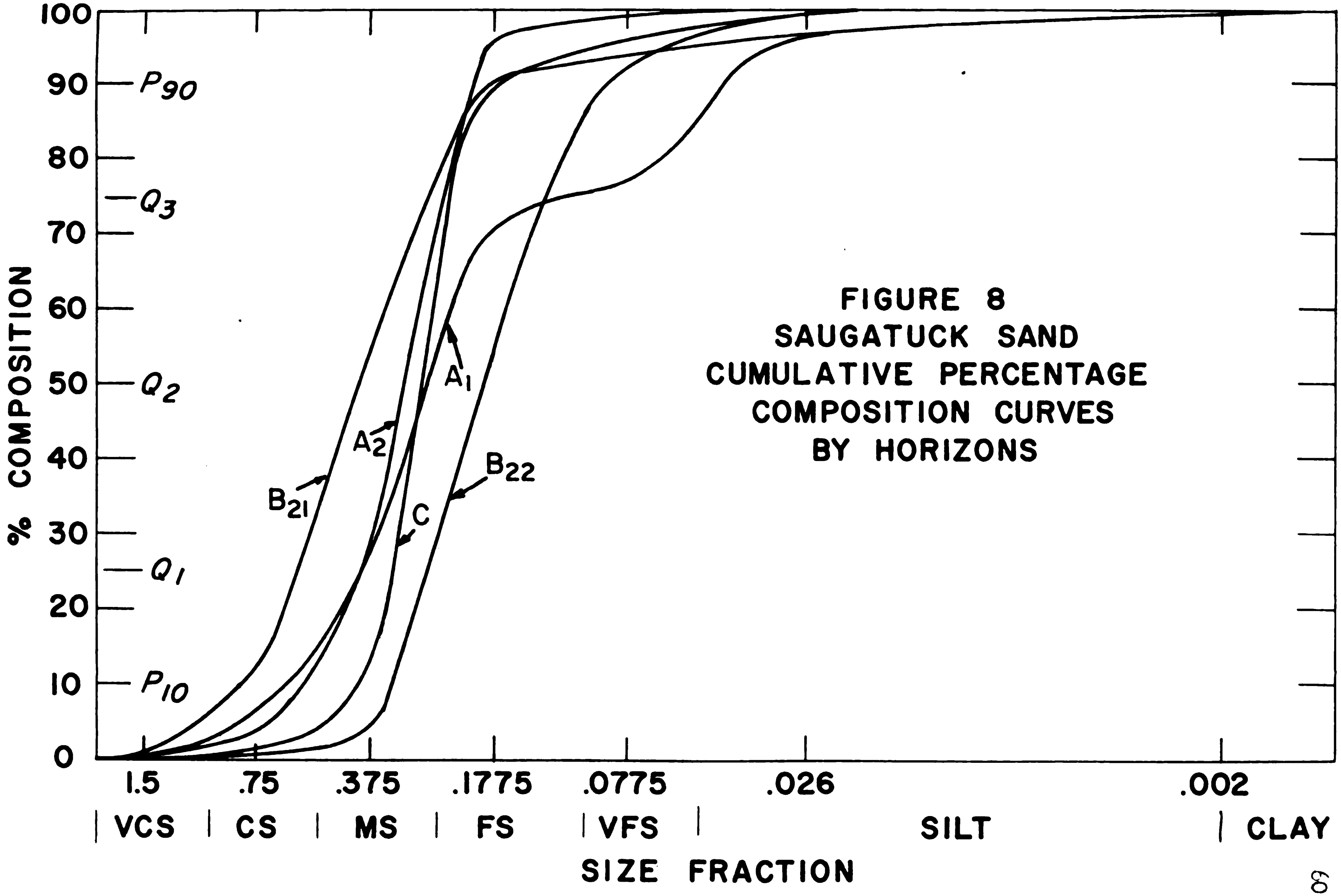


FIGURE 8
SAUGATUCK SAND
CUMULATIVE PERCENTAGE
COMPOSITION CURVES
BY HORIZONS

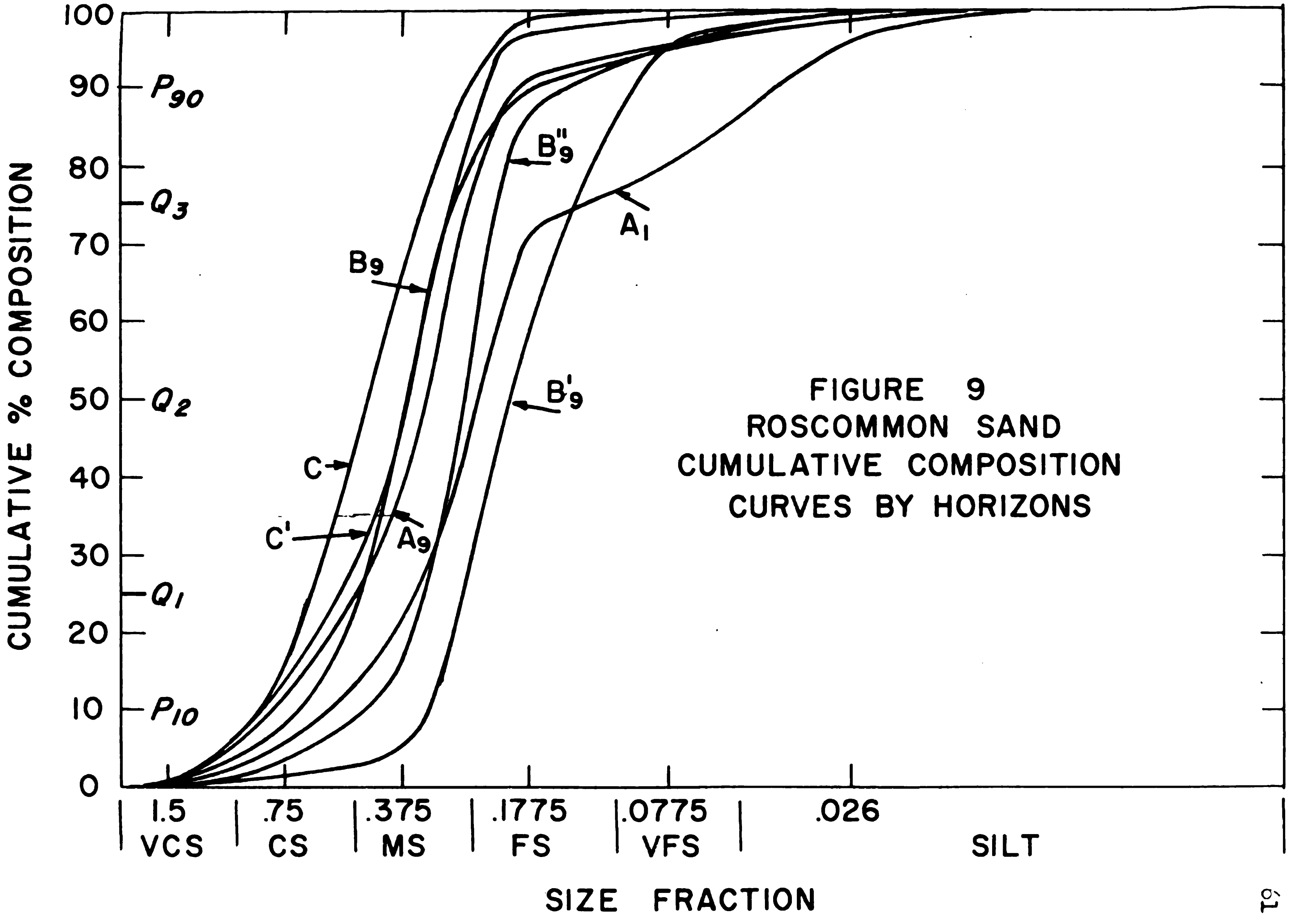


FIGURE 9
ROSCOMMON SAND
CUMULATIVE COMPOSITION
CURVES BY HORIZONS

on the one hand, and for the presence of organisms capable of oxidizing such anions on the other hand.

Organisms capable of oxidizing ferrous iron have been shown to be present in the water of stagnant pools and water pipes etc. (75). It was decided to try and isolate them from the profiles of the Kalkaska and Saugatuck series to find out if they were present in soils as well. Accordingly, in late April 1956, the Kalkaska and Saugatuck sites were sampled again. The procedure used was as follows:

Pits were dug approximately three feet square and deep enough to expose the soil profile. One side of the pit was cut vertically to prepare a fresh face for sampling. The opposite side of the pit was dug out with a slope, thus enlarging the working space. It was decided to sample the A_1, B_{hir}, B_{ir} horizons. Therefore a fresh face was opened on the vertical side of the pit with a knife. Using the volume weights of each soil horizon the volume of soil required to give a 10 gm sample of soil with five samplings was calculated and set on a sampling tool which could be sterilized, and which had been specially prepared for the purpose. A diagram of the tool is shown in Fig. 10. Using the sampler, five samples were quickly transferred asceptically to empty, sterile dilution bottles. The dilution bottles were prepared in the laboratory and after sterilization in an autoclave, they were placed in a tray used for carrying coca cola bottles. The tray facilitated transportation of the dilution bottles to and from the sample site.

The sampler used is made entirely of steel so that it can be

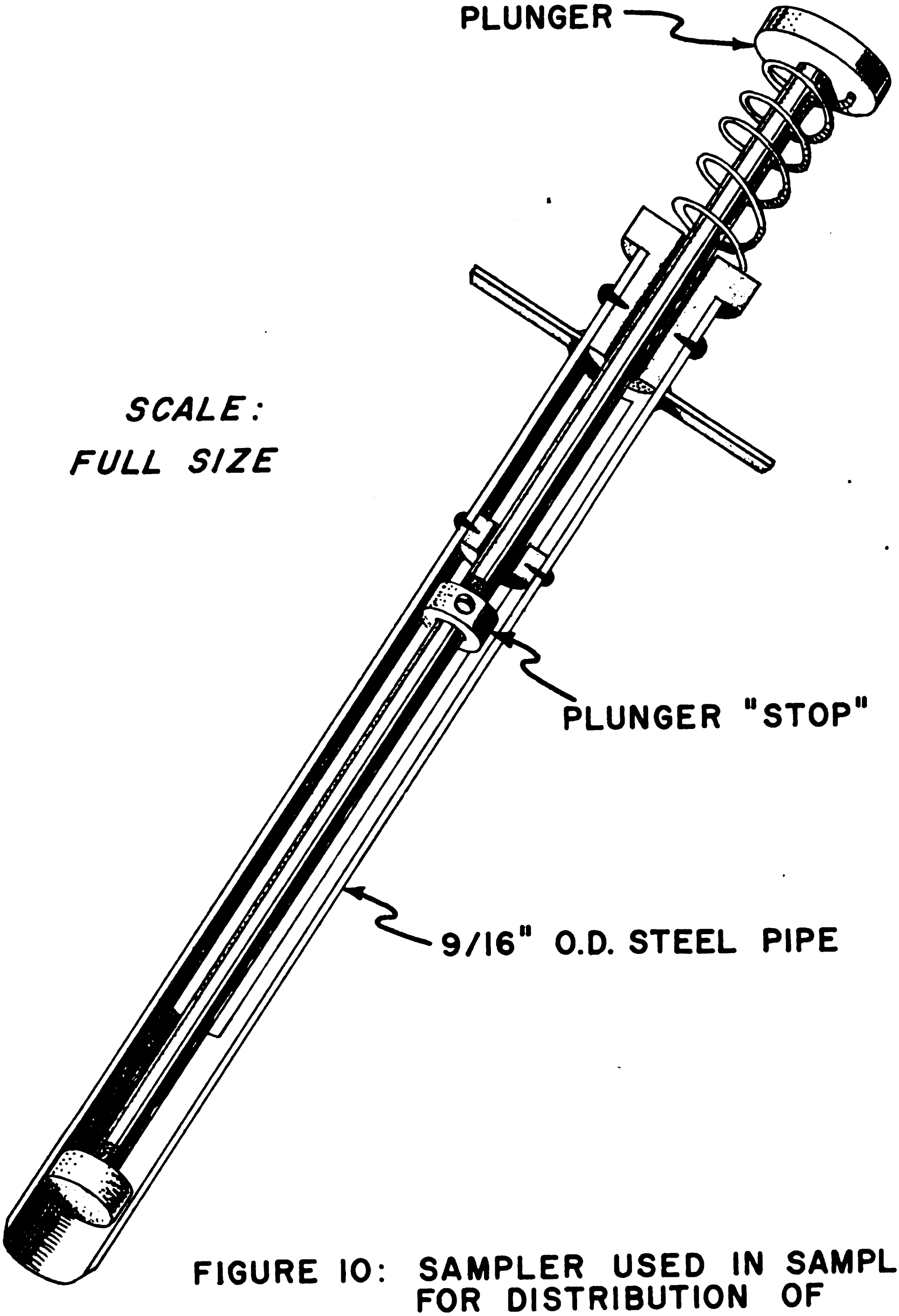


FIGURE 10: SAMPLER USED IN SAMPLING FOR DISTRIBUTION OF MICRO-ORGANISMS.

flamed. Sterilization was carried out by washing in alcohol and flaming in a blow torch flame. In this manner, duplicate samples were collected of each of the required horizons. An additional duplicate set of samples was collected for moisture determinations for each horizon with the sampler set at the same calculated volume. These samples were later dried and weighed and used to calculate the number of colonies per gram of soil. The samples, in field moist condition, were taken to the laboratory where they were suspended in 90 c.c. of sterile distilled water and appropriate dilutions made for counting citrate oxidizing organisms on ferric citrate agar(3).

The dilutions prepared were 1:10T, 1:100T and 1:1M. Inoculations were made and triplicate plates were poured of each dilution on the same day that the samples were taken. The cultures were then cooled and incubated at room temperature for five days. Colonies which formed a brown halo and those which did not were counted separately. Only the brown colonies precipitated iron. The remainder of the organisms used citrate as a source of energy but did not precipitate iron. The reason for this is not understood. The counts for the 1:10T dilution are given in Table I as organisms per gram of soil.

In a second experiment, two iron nails were placed in 500 c.c. erlenmeyer flasks with 200 c.c. of distilled water and glass slides were suspended in the medium with iron wire. After sterilization the flasks were inoculated with 1 c.c. of the 1:10 dilution of the field samples. The cultures were incubated at room temperature for a

Table 1 Distribution of Citrate Oxidizing Organisms in Kalkaska and Saugatuck Profiles

Soil Series and Horizon		Sample	Organisms (Thousands/gm. Soil)	
			Brown	Others
Kalkaska	A_1	126	8.2	63
		125	4.7	27.6
	B_{hir}	124	0.03	1.5
		123	0.03	1.4
	B_{ir}	122	0	0
		121	0	0
Saugatuck	A_1	132	1.7	40
		131	1.5	32
	B_{hir}	130	.04	1.8
		129	0	1.3
	B_{ir}	128	0	0.2
		127	0	0.9

month. Several slides were then examined. No growth was observed, so the incubation was continued. Several months later, the cultures were opened, the slides were removed and treated with dilute hydrochloric acid to remove the ferric hydroxide precipitate. The slides were then stained using the periodate--Schiff's reagent staining procedure described by Lillie (41). Mild periodate oxidation gives rise to aldehyde groupings in microbial cell wall materials and thus provides a basis for the Schiff color reaction. In the preliminary H Cl treatment, the ferric hydrate was not completely removed but pink stained organisms were readily seen. Smears were also made of the voluminous precipitate of ferric hydrate at the bottom of the flasks. After fixing with heat, iron was dissolved with 1:2 H Cl and Gram's iodine applied as a stain. The slides were then examined under the microscope using the oil immersion lense. Results are shown in Table 2.

Table 2 Distribution of Isolates of Filamentous Sheathed Bacteria from Kalkaska and Saugatuck Sands

Series	Horizon	Sample	Observations
Kalkaska	A_1	126	Nothing on incubated slides, very few sheath fragments, empty, on smears.
	B_{hir}	124	Nothing on either slides or smears.
		123	" " " " " " .
	B_{ir}	122	Numerous beaded fragments, apparently branched, on slides.
		121	Short beaded fragments, no branching in smears.
Saugatuck	A_1	132	Nothing on slides or smears.
	B_{hir}	130	" " " " "
		129	" " " " "
	B_{ir}	128	Numerous sheathed, beaded filaments with apparent branching on slides.
		127	Sheathed, beaded fragments in smears.

No positive identification of the organisms observed was made. However, they were very similar to those described by Starkey (75) and by Pringsheim (63). Drawings of the organisms are shown below in Figure 11.

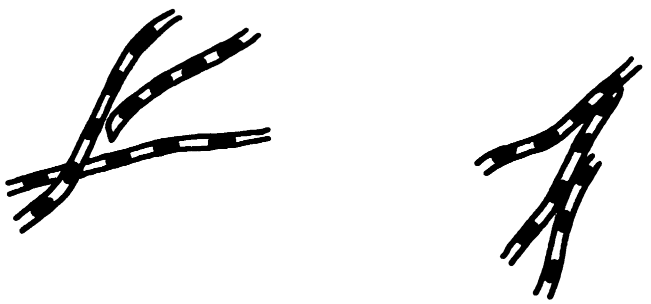


Figure 11. Diagram of Organisms Observed on Slides from the Isolates of the B_{ir} Horizons of Kalkaska and Saugatuck.

Without further study, the organisms observed could not be identified

beyond the family Chlamydobacteriaceae (filamentous sheathed bacteria); but they appeared similar to *Sphaerotilus dichotoma* as illustrated by Starkey (77). The organisms were found without difficulty and were quite numerous on the incubated slides from the B_{ir} horizons; but were absent or found only with great difficulty on slides from the other horizons. The same was true for the smears. No other types of organisms were observed. This indicates that the medium was restrictive for all types of organisms but the ferrous iron oxidizing types.

DISCUSSION

The results of the study on redox potentials are shown plotted by horizons and dates for each of the soils in the hydrosequence in Figures 4, 5, and 6. Statistical analyses by horizons and dates indicate that dates are highly significant. Table 3 shows the statistical analyses of the results from the Kalkaska and Saugatuck series. Table 11 in the Appendix shows the means of the replicates for each soil by horizons and dates.

Table 3. Results of Statistical Analysis of Redox Potentials for Kalkaska and Saugatuck.

Treatment	D.F.	S.S.	M.S.	F.	Nec.F.	
					1%	5%
Dates	13	1,064,662	81,897	14.34	2.23	1.77
Horizons	8	1,017,680	12,721	2.23	2.65	2.01
Error	104	594,009	5,712			
Total	125					

L.S.D. for dates - 71.2 millivolts

L.S.D. for horizons - 57.2 millivolts.

A chi-square test of the variance of the A_1, A_g and B''_g horizons of the Roscommon series indicated that an uncontrolled factor was affecting the potentials in these horizons. This was not true of the other soil horizons. Therefore, the three horizons were analysed for significance between replicates. The results of the analysis are shown below in Tables 4, 5 and 6.

Table 4. Analysis of Variance of the A_1 Horizon of the Roscommon Series.

Treatment	D.F.	S.S.	M.S.	F.	Necessary F	
					1%	5%
Replicates	4	155,999	38,999.8	19.95	2.43	1.88
Dates	14	6,698,899	478,493	244.8	3.68	2.54
Error	56	109,463	1,955			
Total	84					

Table 5. Analysis of Variance for the Ga_{-1} Horizon of the Roscommon Series.

Treatment	D.F.	S.S.	M.S.	F.	Necessary F	
					1%	5%
Replicates	4	293,641	73,410	3.18	2.43	1.88
Dates	14	4,288,477	306,320	13.3	3.68	2.54
Error	56	1,294,241	23,111			
Total	84					

Table 6. Analysis of Variance in BG_{-1} Horizon in the Roscommon Series.

Treatment	D.F.	S.S.	M.S.	F.	Necessary F	
					1%	5%
Replicates	1	147,298	147,298	28.14	8.86	4.60
Dates	14	3,238,795	231,343	44.19	3.70	2.48
Error	14	73,287	5,235			
Total	29					

The variance between replicates in all three horizons is significant. Due to the small thickness in the BG_{-1} only two electrodes were successfully installed there. The F values for replicates in this horizon is larger than in the other two horizons where five replicates were used. This suggests that more replicates should be used. Increasing the number of replicates would allow more degrees of freedom and thereby reduce the mean square values for the replicate comparisons. It is also interesting that replicates are more variable in the A_1 horizon than in the AG_1 horizon. This suggests that the variance is connected in some way with organic matter. The activity of microorganisms, varying from place to place in the horizon could be responsible. The effect of excess water was no doubt also a contributing factor. There may have been leakage in the insulation of some of the leads. Damage to the electrodes during installation is not a contributing factor in this case, however, since the surface horizons are most effected and they would receive the least damage during installation. Another contributing cause to the variance between electrodes in the A_1 horizon may have been the effect of alternate freezing and thawing in the spring season which resulted in some heaving of the electrodes. Analysis of variance of the redox potentials observed in the soil at the Roscommon site is shown by itself in Table 7. Differences in

Table 7. Analysis of Variance of the Roscommon Series.

Treatment	D.F.	S.S.	M.S.	F.	Nec. F	
					1%	5%
Horizons	5	429,151	85,830	3.11	3.29	2.35
Dates	14	1,995,638	142,546	5.16	2.35	1.84
Error	70	1,934,081	27,630			
Total	89	4,358,870				

redox potentials between horizons are significant as are differences between dates.

In the analysis of variance for the three soil series there were significant differences between dates at the 1% level and between horizons at the 5% level.

It was suggested, that since there is a cyclic variation in the redox potential due to climate, the results are skewed rather than symmetrically distributed about the mean. It was therefore decided to select a series of dates in one season for analysis. Three dates of the winter season of 1953 and 1954 were used.

Table 8. Analysis of variance for 3 dates during winter of 1953-54 for Kalkaska and Saugatuck Profiles.

Treatment	D.F.	S.S.	M.S.	Nec. F.	F
					1%
Horizons	8	591,515	73,939	60.41	3.89
Dates	2	12,035	6,018	4.92	6.23
Error	16	19,577	1,224		
Total	26	623,127			

It can be seen that analysis of variance of results for only three dates tends to increase the significance of horizons and reduce the significance of dates. Examination of Figures 4, 5, 6 shows that some horizons vary more than others so that the graphs for individual horizons tend to cross. Results for horizons should therefore be comparable, although the absolute values for the redox potentials no doubt vary somewhat from the true values. Such variation is included in the error term. Variation with season or climate, indicating seasonal trends in redox potential, should be representative regardless of the possible variation of the absolute redox values from the true values. Table 14 in the Appendix shows the redox potential for a number of oxidation-reduction couples that exist in soils. They are shown compared to the calomel electrode and adjusted to pH 5.0 using the Nernst equation. Values used were obtained from Latimer (38). Examination of these equations shows that all E_c values fall within the range of redox potentials measured in the Kalkaska, Saugatuck and Roscommon series.

Figure 12 shows a comparison of the moisture determinations for Saugatuck and Roscommon series with redox potentials. The moisture contents of both series were measured with nylon blocks (16) and are therefore comparable. The moisture variations for the Kalkaska series were measured with plaster of paris blocks. They are not shown plotted since they are not comparable to those obtained for the Saugatuck and Roscommon series which were measured with nylon blocks. Study of the values in Table 13 of the appendix shows that the Kalkaska series behaved similarly although it was better drained at

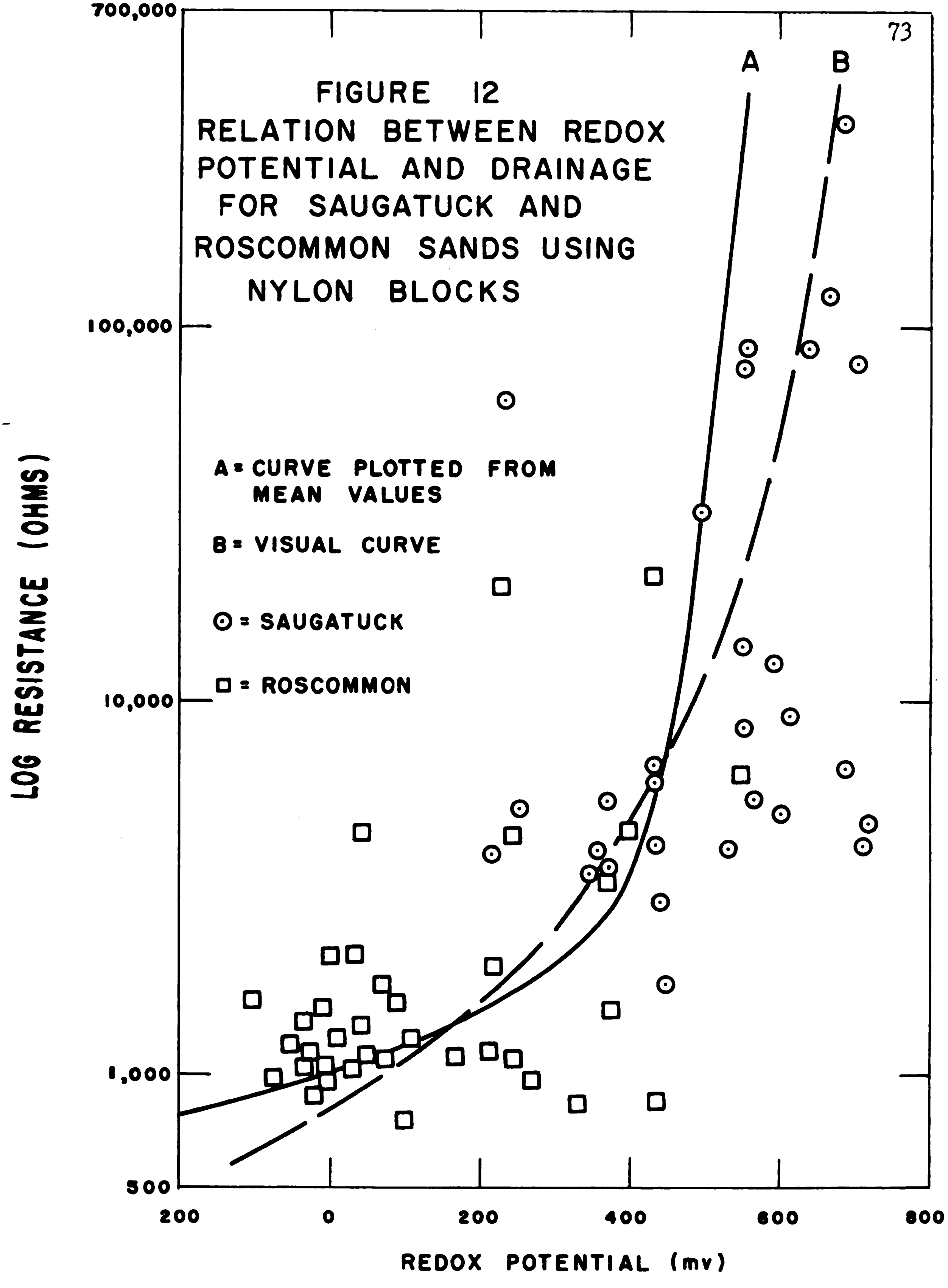


FIGURE 12
RELATION BETWEEN REDOX POTENTIAL AND DRAINAGE FOR SAUGATUCK AND ROSCOMMON SANDS USING NYLON BLOCKS

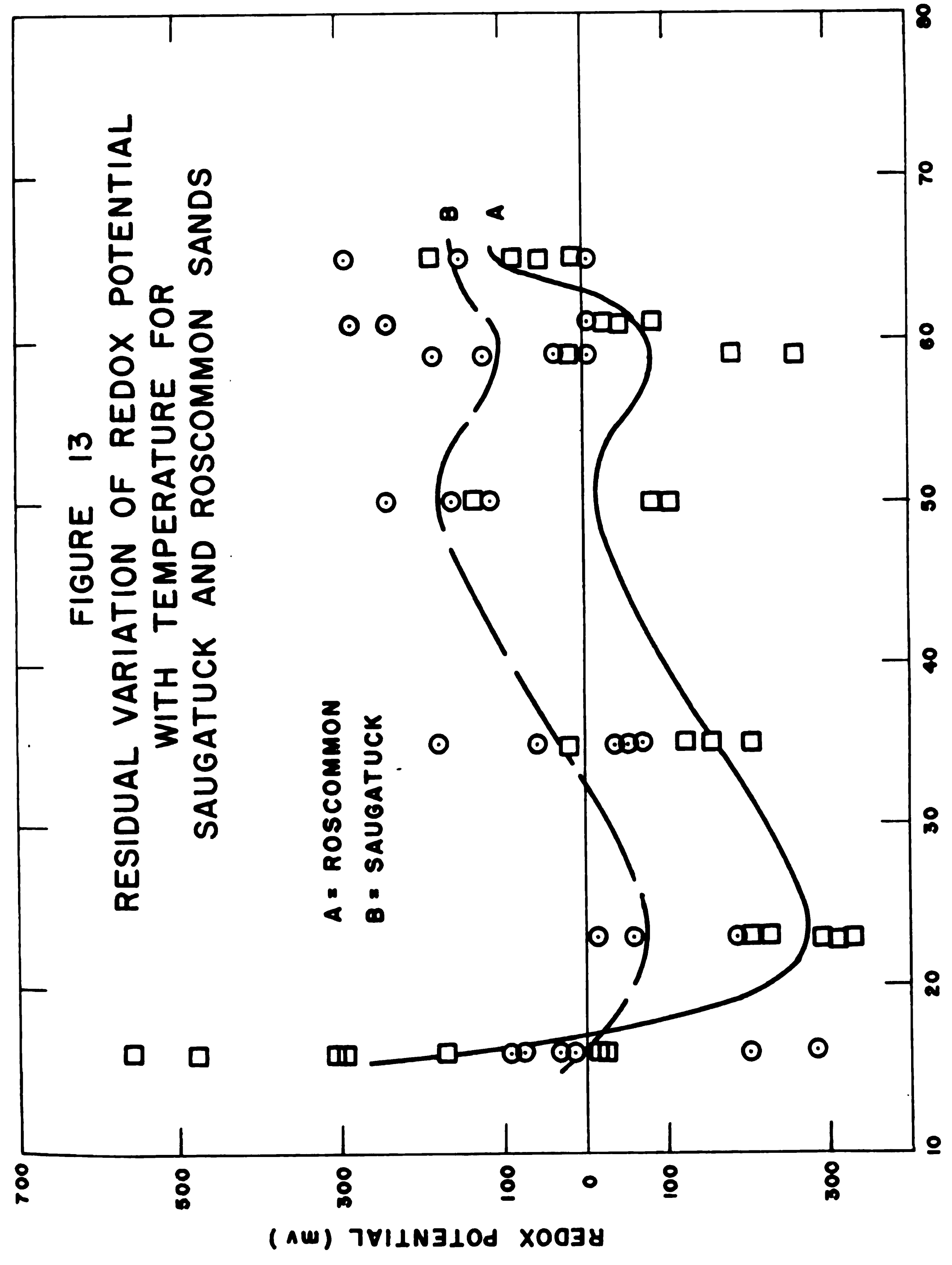


FIGURE 13

RESIDUAL VARIATION OF REDOX POTENTIAL WITH TEMPERATURE FOR SAUGATUCK AND ROSCOMMON SANDS all times. Since the moisture content changes only a small amount for a large change in resistance of the nylon blocks, the moisture meter readings are shown plotted as the logarithm of the block resistance in ohms rather than as actual moisture percentages. It can be seen that there is a general relationship between redox potential and the moisture content of the soil. These results suggest that relief and climate have a great influence on the oxidation-reduction status of the soil. Table 15 (appendix) shows the rainfall and temperature at the Cadillac station for the years 1953, 1954 and 1955 over the period that the experiment was in progress. The data were obtained from Climatological Data for the Michigan section for the period from 1953 to 1955 published by the U. S. Weather Bureau. The Cadillac station is approximately fifteen miles from the experimental site and therefore should be fairly representative. The residual variation in the redox potentials from the mean curve A for the Roscommon and Saugatuck series are shown plotted in Figure 13 against the mean temperature for the two week period prior to the date of the reading. An asymmetrical sine curve was obtained which indicates that a great part of the variability (residuals) in redox potential about the mean moisture line in Figure 12 was due to temperature variation. Examination of the results from Figures 4, 5, 6 suggest that the climate greatly affects the redox potential of the soil and that both moisture and temperature should be measured in conjunction with redox potentials.

The remaining residual variation not due to temperature is no doubt due largely to soil variation. Note also that the curves in

Figure 13 show a sharp dip at the high temperature end. The activities of microorganisms are probably responsible for the high temperature dip in this curve. Since microorganisms would be most active during periods when moisture was favorable as well as temperature, one would expect that they would be most active in the spring and fall when the soil was both moist and warm (above 50°F). The low potentials observed while the temperature was low (50°F or lower) are probably due in large part to chemical reduction in the soil rather than to the activities of microorganisms. It was observed that at no time during the course of experiment was the soil frozen. During the winter period while it was covered with snow it was also moist. Thus, the late winter and early spring period is the most favorable time of year for chemical reduction due to the presence of a fresh supply of water soluble plant materials from the previous summer's vegetative growth, high moisture and rising temperatures. This may account for the sudden drop in the redox curve around 20°F air temperature (in early January) shown in Figure 13.

However some organisms may be active at these low temperatures. Certain psychrophilic(cold loving)organisms include some of the iron oxidizing bacteria described by Starkey (75) and Pringsheim (63, 64).

The results of the microbiological studies indicate that iron oxidizing organisms were present in the B_{ir} horizons of both the Kalkaska and Saugatuck series. According to Starkey, some of the organisms are most active at temperatures ranging from 32°F to 70°F. For Gallionella the optimum temperature is given as 43°F. The organisms observed grew under aerobic conditions since they were distributed most densely on the glass slides near the surface of the distilled water in the iron medium of the second experiment. The falsely branched filaments observed however were more like the type described by Starkey as <u>Sphaerotilus</u> <u>dichotoma</u>.

According to Starky, these organisms obtain energy from the oxidation of ferrous iron in accordance with the following reaction (75):

$$4\ \mathrm{Fe(HCO_3)_2} + \mathrm{2H_2} + \mathrm{O_2} \rightleftharpoons 4\ \mathrm{Fe(OH)_3} + \mathrm{8CO_2} + \text{energy.}$$

In the absence of organic materials they utilize the carbon from dissolved CO_2. The above reaction suggests that the mineral siderite ($FeCO_3$) or some other form of iron carbonate may be present in the B horizons of podzols. These results are interpreted as evidence that under the conditions observed in the soils under study, iron oxidizing organisms were present in the soils and could be active in the development of the Podzol B horizons. Examination of the results from the first experiment (Table 1) indicate that organisms in detectable numbers were present in the A_1 and B_{hir} horizons which could oxidize the ferric citrate and precipitate ferric hydroxide or which could utilize citrate as a source of carbon or energy without precipitating iron. The ability to utilize citrate as the sole energy source is sufficiently limited among bacterial species to permit its use in selective media for isolating certain nutritional groups (55). Although the evidence is not highly specific, the presence of organisms capable of utilizing ferric citrate, with or without iron precipitation, on artificial media infers the presence of appropriate substrates in the soil horizons studied. The numbers of organisms recovered on ferric citrate agar provide indirect evidence that citrate or related tricarboxylic and dicarboxylic acids may be included among the native substrates present in these soils. Both ferrous and ferric iron are known to form complex compounds with many of these materials (6, 14, 72, 73, 89). Iron tends to be reduced on forming complex organic compounds in the soil (6, 14), therefore it is to be expected that iron in solution is present in both the ferrous and ferric state. It has been observed here that citrate utilizing organisms are most numerous in the A_1 horizons, present in the B_{hir} horizons and absent, or very scarce, in the B_{ir} horizons of the Kalkaska and Saugatuck series. This suggests that many of the iron complexes formed in the A_1 horizons are decomposed there and some are carried to the B_{hir} horizon before they are utilized by microorganisms. Some of the iron, mobilized in the A horizons, must therefore be released into solution in the free state either as the ferrous or ferric form in the A and upper B horizons. It has also been observed here that iron oxidizing organisms are present almost exclusively in the B_{ir} horizons of both soils. This means that ferrous iron must be present in the B_{ir} horizon in sufficient amounts to serve as the source of energy for the iron oxidizing bacteria. The mobilization of iron oxides in the A horizons of podzols by the formation of water soluble complex organic compounds accompanied by reduction of some of the ferric iron to the ferrous form, the release of the ferrous and ferric iron in the free state through decomposition of the organic complexes by microorganisms in the A and B_{hir} horizons, translocation of the mobilized materials to the region of the B_{ir} horizon by percolating waters, and precipitation of the free ferric iron there by iron oxidizing organisms is a possible mechanism of Podzol formation.

Mechanical Analysis

Results of the mechanical analyses show that all three soils were essentially sands. Both the Saugatuck and Roscommon sites were somewhat more stratified than the Kalkaska site, see Table 12 in the Appendix and Figures 7, 8, and 9 in the text. This suggests that there has been some soil loss from the Kalkaska site by erosion and some soil gain at the Saugatuck and Roscommon sites as a result of erosion of the surrounding areas or that the materials were originally more stratified at the Saugatuck and Roscommon sites. To further substantiate this observation, there is a relative loss in silt and very fine sand in the Kalkaska and an enrichment in coarse sand, while the Saugatuck and Roscommon series show a relative gain in very fine sand and silt and a relative decrease in coarse sand. However all soils show a trend to increasing amounts of fine or medium sand with depth in the profile. Comparison with the redox profiles suggests that the variation in porosity due to differences in texture as a result of stratification is not the determining factor as far as the redox profile is concerned. The redox profile correlates better with the organic matter distribution, the degree of oxidation in the B horizon, and the variation in moisture content as determined by the rainfall and the season. Such variations in texture may contribute somewhat to the experimental error. The variations shown in texture are not so great that the poorly drained or the imperfectly drained soils would be considered different from the Kalkaska series and not included in the catena or hydrosequence. The presence of charcoal in the A horizon of the Kalkaska series indicates that a forest fire passed over the area. There has also been some accumulation of clay in the A_1 and B horizons of all three soils. The color of the A_2 horizons of many podzol sites in northern Michigan is pinkish gray (7.5 YR 6/2). As a matter of interest, on dispersion of the soil samples during mechanical analyses, the pinkish gray color remained in the suspension after the sands and silts had settled out. This indicates that the pinkish gray color is associated with the thin coating of clay on the sand particles.

The Moisture Measurements

Examination of the data for the Kalkaska site shows that at no time in the period of the study did the moisture content of the profile exceed 4% of the dry weight of the soil (16). This means that about 12% of the pore space was filled with water and suggests that aerobic conditions existed in the profile at all times. On the same basis, the Saugatuck was approximately 20% saturated at its wettest point and the Roscommon approximately 40% saturated. The figure for the Roscommon seems low because the site was covered with water at times when the measurements were taken and the soil should have been nearly 100% saturated. Examination of the weather data for the period over which the moisture measurements were made shows that there was a deficiency of 3.65 inches of rainfall on January 1, 1954 and an excess of 2.98 inches by April 30, 1954. This means an increase in the water content of the soil during the period which was observed while the moisture blocks showed a decrease. The weather data also shows a net difference of 6.57 inches of water in the four months of the fall of 1953 as compared to the fall of 1954. This difference in rainfall caused a difference in the amount of water on the Roscommon site and was reflected in the redox potential for all three sites during the winter months (see Figure 6).

The Redox Profile

The analysis of variance indicates that there are significant differences in the redox potentials between horizons. The A horizon of the Kalkaska site was lowest of all the horizons in the Kalkaska profile except during the winter of 1954 and 1955. Then the A_2 horizon and the B_{hir} horizon were lower. At all times the B_{ir} and the C horizons were significantly higher than the other three horizons.

The redox profile suggests that ferrous iron, moving downward in the percolating water from horizons of low redox potential, was oxidized to ferric iron as it entered the region of higher redox potential. According to Latimer (38) the ferrous-ferric couple as shown by the equation,

$$Fe^{2} \rightleftharpoons Fe^{3} + e$$

has an E_h of -771 millivolts. Compared with the saturated calomel electrode at pH 5.0 the E_c would be -526 millivolts. The negative sign means that the couple tends to go spontaneously to the left or to the reduced side and that the couple tends to be more oxidizing than the calomel electrode. In order to make the value positive the equation should be reversed as follows.

$$Fe^{3} + e \rightleftharpoons Fe^{2}$$

This means that a large amount of energy is required to remove the third electron from the iron atom and suggests that some other mechanism of oxidation of ferrous iron may be more important in soils. The formation of water soluble iron-organic complexes tends to reduce the amount of energy required to remove the third electron (72), and would make the ferrous iron more susceptible to easy oxidation. The mechanism called valence induction described by Selwood (71) and mentioned by Bloomfield (5) would also cause the oxidation of ferrous iron to take place more readily. Merkle (50) discussed the work by Peters (60) with ferrous and ferric iron. According to this work, the E_h of the ferrous-ferric couple is 713 millivolts. Comparing with the saturated calomel electrode at pH 5.0 the E_c of the ferrous-ferric couple would be 468 millivolts. This value is comparable to Latimer's value of -526 millivolts. It differs numerically from Latimer's value because of the different E^o values used and differs in sign because the conventions in the European system were used by Peters. At the potentials observed in the A and B horizons of the Kalkaska site, the ferrous-ferric couple could have been operative there during most of the time of

the study except for the winter of 1954-55. The same couple could have been operative in the A_2 and B_{hir} horizons in the Saugatuck site. Potentials in the B_{ir} horizon of the Saugatuck site were too low for the ferrous-ferric couple to have been operating. Therefore some other couples would have to be active. The oxidation-reduction couple (38)

$$Fe(OH)_2 + OH^- \rightleftharpoons Fe(OH)_3 + e$$

has an E_c of 274 mv. at pH 5.0, or the couple

$$* \ 2Fe^{2} + 6OH^- \rightleftharpoons 2Fe(OH)_{3(S)}$$

which has an E_c of 80 millivolts at pH 5.0 could have been operative at lower soil redox potentials.

Under the aerobic conditions observed in the soil at the Kalkaska and Saugatuck sites the $Fe^{2} \rightleftharpoons Fe(OH)_3$ couple cited above does not determine the E_c of the soil. In the presence of sufficient hydroxyl ion, the ferrous iron content of the soil would be very small since it would tend to be converted quickly to ferric hydroxide. According to the literature (51) this process could be important at pH values higher than 5.0. Under the conditions observed in the soil at the Roscommon site the couple could be active in the weak GB-1 horizon found there and this reaction may help to explain the highly mottled zone observed in many poorly drained soils. It also suggests that soil redox potentials should be lower than 80 mv before the gley process becomes strongly active.

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*Calculated from the solubility products of Fe^{2} and $Fe(OH)_3$ using Latimer's convention.

According to Latimer (38) the ferrous-ferric couple tends to go spontaneously in the direction of the ferrous ion. That is the ferrous-ferric couple tends to be oxidizing under acid conditions. In order for the couple to be reversed so that ferrous iron is converted to the ferric state, a strong oxidizing force is necessary. On the other hand, Merkle's (50) discussion indicates that the ferrous-ferric couple could contribute to the E_c of the soil. In fact, at potentials approaching 600 millivolts, it indicates that the iron would be 99% or better in the ferric state at pH 5.0. Under conditions of good aeration in the soils at the Kalkaska and Saugatuck sites such potentials were observed.

The strong oxidizing force required to drive the ferrous-ferric couple to the ferric side could be provided by oxygen in well aerated soils and also by the iron oxidizing organisms found to be present in the B_{1r} horizons of both soils in this study.

Manganese is commonly present in soils and is strongly oxidizing. Manganese dioxide (MnO_2) is a common form of manganese in soils. Therefore, one would expect the following couple to be active.

$$MnO_2 + 4H^{+} + 2e \rightleftharpoons Mn^{2} + 2H_2O$$

Compared with the calomel electrode and adjusted to pH 5.0, the E_c of this cell is 495 millivolts. This means that manganese is also an important contributor to the redox potential in soils, and since it is oxidizing by nature, it may determine the redox potential of the soil at times and could provide an oxidizing force for iron.

According to the results of the redox potential studies in the soils at the Kalkaska and Saugatuck sites, the degree of aeration is also important in determining the redox potential of the soil. The effects of variations in aeration are also well demonstrated at the Roscommon site. Since oxygen is the important element concerned with aeration of soils, an oxygen couple may be important. The following couple:

$$\tfrac{1}{2}O_2 + 2H^+ + 2e \rightleftharpoons H_2O$$

has an E_c of 689 millivolts at pH 5.0.

This oxygen couple therefore falls within the range of the redox potentials observed in soils and suggests that oxygen is also an important contributor to the redox potential of the soil. Since the oxygen content of the soil varies widely as affected by the amount of water present in the soil and the amount of carbon dioxide in the soil atmosphere, this couple could be responsible for the high potentials observed in the soils during the periods of good aeration and could account for the wide changes observed in the redox potentials. This type of variability is closely related to climate and microorganisms which are the active factors of soil formation (32). The effects of these factors have been shown in Figure 11 and 12.

In this soil study, the redox potentials observed ranged from approximately 750 millivolts on the positive side to -300 millivolts on the negative side. According to Merkle (38) this is about the normal range in soils. Oxidation-reduction couples which operate outside of this range may not be operative in soils.

Therefore, the study of redox potentials can be useful in serving as an aid to point out certain reactions which may be operative in soils and which may determine the redox potential of the soil at times. The evidence discussed here is inconclusive and further studies should be carried out to determine the effects of the oxidation-reduction processes that go on in soils and to clarify the mechanics of the weathering processes involved in soil genesis. They may be useful in soil fertility studies also.

In the soil profile, redox potentials are a measure of the intensity of the oxidizing or reducing tendencies. The amount of material in the soil that is oxidized or reduced depends on the magnitude of the oxidizing or reducing force and the length of time that the force is operative. It also depends on the amounts and kinds of materials available, their chemical nature and the rate at which the redox reaction proceeds once it is initiated. This serves to explain why low redox potentials may be observed in a soil for a short time with little effect on the soil characteristics as in the Saugatuck and Kalkaska while low potentials present for long periods are observed in soil profile characteristics as in the Roscommon site. The amount of material oxidized or reduced can be measured with a strong oxidizing or reducing agent. Since oxidizable and reduceable materials are continually being added to the soil through additions of organic matter and inorganic materials, and at the same time other materials are being removed by leaching processes, the measurement of the total amount of oxidizable or reduceable material by simple titration cannot be of much use. Rather, effects on specific materials should be studied and measured periodically to follow changes that occur. The change in redox potential as it varies with changes in soil temperature, moisture content of the soil, aeration of the soil, and microorganisms can serve as a guide to point out suitable dates for sampling.

Examination of Figure 13 shows that temperature affects the redox potential of the soil. The absolute temperature factor in the Nernst equation determines the effect of temperature on redox systems being measured. According to Michaelis (52) this factor amounts to about one millivolt per degree over the range of temperatures in which this study was carried out and that it varies directly as the temperature. In this study the temperature ranged from about 0°C to 30°C which would amount to about 30 millivolts and would tend to overemphasize the redox potentials observed in the soil at the higher temperatures. This variation is within the limits of the error term in the statistical analysis. The more important effects of temperature is the indirect effect on the redox potential through microorganisms and vegetation.

Examination of Figures 4 and 5 shows that the redox potential of the A_1 horizon of the soil at the Kalkaska site was significantly lower than that of the underlying horizons. In addition, the redox potential of the B_{hir} horizon was lower than the overlying A_2 horizon and the underlying B_{ir} horizon. These results are due to the effect of the organic matter in those horizons. The result could be due to the activity of microorganisms (27) or to the formation of ferrous or ferric complexes with organic complex forming materials (51). According to Bloomfield (5, 14) a large part of the ferric iron was reduced to ferrous iron during the process of complex formation. If the ferrous-ferric couple was determining the redox potential of the soil, one would expect the redox potential to be lowered under such conditions.

If the reducing effect of the organic matter in the A_1 horizon was strong enough to cause reduction in the presence of oxygen to account for the low potentials observed there, the mechanism could operate in the B horizon under aerobic conditions and give rise to high potentials. The thickness of the A_2 horizon would then be a measure of the intensity of reducing conditions in the A_1 horizon, and would vary with the kind of organic matter in the A_1 horizon, the activities of microorganisms present in the A_1 horizon, and the effect of moisture which would be related to the micro relief. This agrees with the observations of Lag and Einevoll (37). The degree of development of the B horizon would be a function of the reducing intensity in the A_1 and A_2 horizons, the amount of leaching, and the amount of the sesquioxides present in the A horizons that were susceptible to the mobilization process. Such a process would lead to the development of an incipient A_2 and B_2 horizon in a youthful soil; and a gradual development of both horizons downward until equilibrium with the environment was reached. The soil profile would then have reached maturity. This also agrees with observation in the field (68).

The redox profile at the Saugatuck site is the reverse of the one at the Kalkaska site. The observed potentials in the A_1

horizon of the Saugatuck site are highest from April through August. This correlates with the period of maximum growth of the vegetation. In this site, the aspen feeding roots were concentrated in the A horizon due to the impervious nature of the "ortstein", and the presence of a high water table. In the Kalkaska site there was no concentration of tree roots in the A horizon. This suggests that the plant roots, by removing the water from the soil through transpiration, were improving the aeration of the A_1 horizon. Improved aeration caused oxidation of the reduced substances there and raised the redox potential. The low potentials observed in the B_{1r} horizon were due to the high water table. Because of the hardness of the ortstein in the Saugatuck profile, it was not possible to put electrodes into the C horizon. No results were therefore obtained for the C horizon of the Saugatuck site. The low potentials observed during the winter of 1954 and 1955 were probably due to the excess moisture, and during this time the redox potential of A_2 and B_{hir} horizons dropped below that of the B_{1r} horizon.

The characteristics of the soil profile at the Saugatuck site, were such that they suggested a soil forming process similar to the one at the Kalkaska site. The redox potentials in the A_1 horizon of the Saugatuck were the highest observed in the profile. Such results suggest that the process of mobilization of sesquioxides is one which can operate even under strongly oxidizing conditions. The process of iron-organic matter complex formation could have been in operation however and microorganisms were also active as is indicated by the experiment on citrate oxidizing organisms in both the A_1 and B_{hir} horizons. The degree of development of the B_{hir} and B_{ir} horizons suggest that more materials had been deposited there than could be accounted for by the normal downward leaching process.

In the spring of 1956, when the site was sampled for the study of microorganisms there was lateral movement of water through the B_{ir} horizon along a moisture gradient. This movement no doubt occurred whenever the water table was high and could have contributed to the accumulation of sesquioxides deposited in the B_{ir} horizon. Although the redox potentials of the B_{ir} horizon were lower than those in the horizons above, conditions were still suitable for the deposition of sesquioxides, since an ortstein had developed there. The iron oxidizing bacteria may have been a contributing factor.

The analysis of variance of the results from the Roscommon site indicate that only the C and BG_2 horizons were significantly different from the other horizons. Since these horizons were the deepest in the profile, they were probably affected longest by the high water table. The upper horizons were affected by oxidizing conditions for some of the time during the summer months. The higher potentials observed during the winter of 1953 and 1954 were due to the lack of excess moisture which was pointed out in the discussion on rainfall. In both summer seasons the potentials tended to rise as the soil aeration improved. The lowest potentials were observed during the month of June. This time corresponds to the season when the temperature and moisture conditions favored the activities of

microorganisms. In the case of the Roscommon site anaerobic conditions were dominant and strong reduction occurred, while at the Saugatuck and Kalkaska sites, aerobic conditions prevailed and the redox potentials rose.

The oxidation-reduction systems in the soil which are dependent on the aeration status of the soil and are important in soil fertility, must change their oxidation state as the redox potential of the soil changes with conditions of climate and drainage. The use of drainage, irrigation and other management practices which help to control the redox potential of the soil are thus important in soil fertility. The importance of organic matter in changing the oxidation state of the soil constituents has been established. However, very little is known about the organic redox couples that may be important in affecting the redox state of the soil. An effort should be made to discover the nature of such couples.

SUMMARY AND CONCLUSION

A technique was devised for the measurement of redox potentials in the soil in all seasons of the year. Using this technique the change in oxidation-reduction status of Kalkaska, Saugatuck and Roscommon series, a hydrosequence of soils, was followed for a period of two years extending from September 1953 to August 1955. It was established that the variation in redox potential with time correlates with the moisture content of the soil and with the prevailing air temperature prior to the time of the measurements. A more exact comparison would no doubt be obtained by measurement of soil temperature. It was also established that there is a redox profile in the soil which is related to the soil horizons. Conditions were oxidizing for iron in the B horizons of Kalkaska and Saugatuck in all seasons, but were not for the Roscommon series. A study of the distribution of citrate oxidizing microorganisms in the profile of the Kalkaska and Saugatuck series was carried out. Microorganisms capable of oxidizing ferrous iron to ferric hydroxide have been isolated from the B_{1r} horizons of the Kalkaska and Saugatuck series. The data suggest that iron oxides may be mobilized by reduction and the formation of organo-metallic complexes in the A horizons of podzols and that the complexes may be decomposed by microorganisms there, releasing the ferrous or ferric iron into solution. The presence of the redox profile indicates that the ferrous iron was oxidized in the B horizon and there precipitated or adsorbed by the ferric hydroxide already present and then oxidized by the process of valence induction as suggested by

Bloomfield (12). These results do not eliminate the possibility that movement of sesquioxides in colloidal form such as clay humates, or as clay iron complexes, takes place and that they can be precipitated at the isoelectric point of the colloids. It is concluded that several processes including the washing of dispersed clay particles downwards by percolating waters may be active in the development of podzol B horizons.

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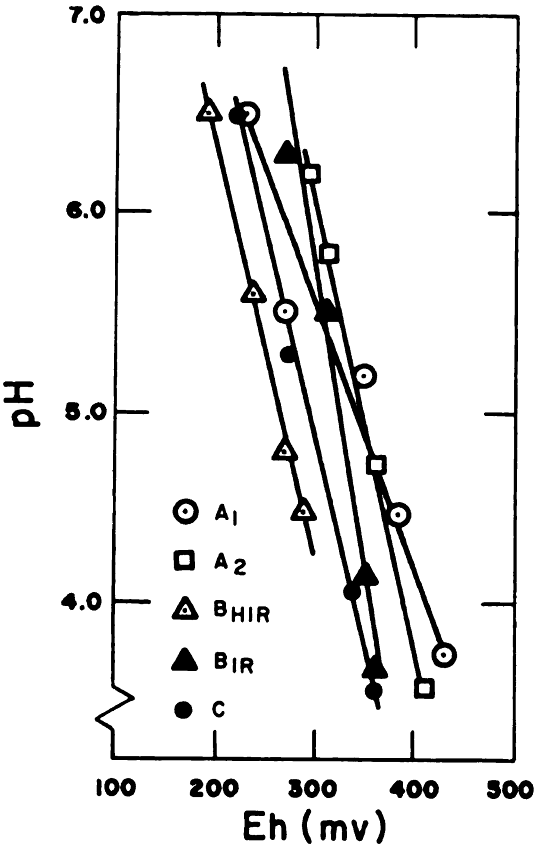
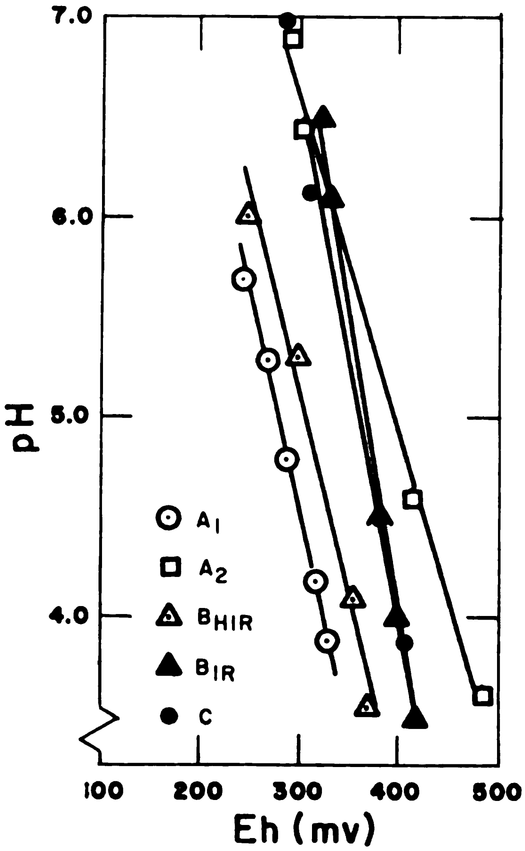
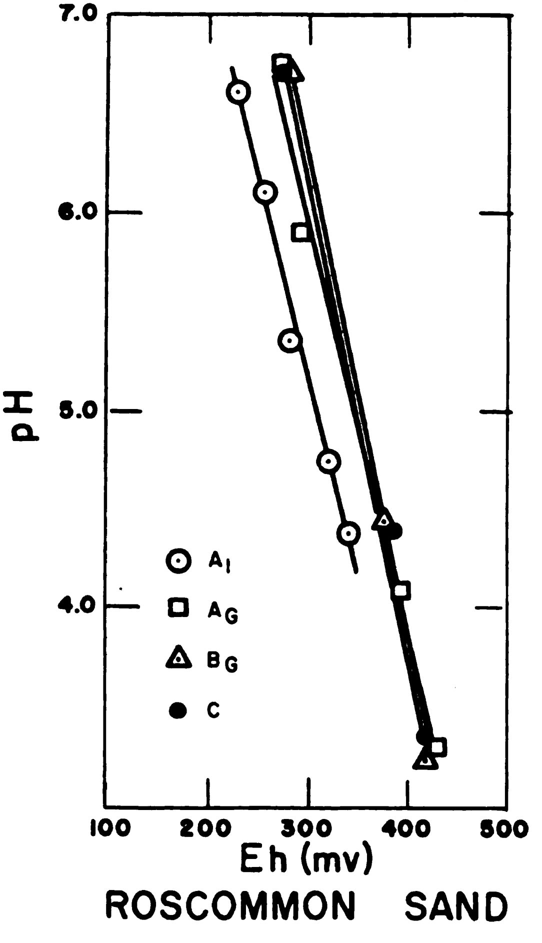
APPENDIX



KALKASKA SAND



SAUGATUCK SAND



ROSCOMMON SAND

FIGURE 14
Eh-pH CURVES
FOR
KALKASKA, SAUGATUCK
AND ROSCOMMON SAND
BY HORIZONS

Table 9 Mechanical Analysis
Percent Composition by Separates

Soil Series	Horizon	2- 1.0	1.0- 0.5	0.5- 0.25	0.25- .105	.105- .05	.05- .002	.002	Total
Kalkaska	A_1	0.26	10.12	33.14	42.18	4.69	6.42	3.19	100
	A_2	0.26	9.66	34.96	49.83	2.70	1.49	1.10	100
	B_{hir}	0.27	6.46	30.75	58.20	1.57	2.75		100
	B_{ir}	0.14	4.55	30.30	61.40	2.41	1.31		100
	C	0.20	3.23	18.8	73.0	4.17	0.42		100
Saugatuck	A_1	0.13	6.1	19.45	44.60	6.95	18.90	4.0	100.13
	A_2	0.32	3.55	26.0	58.80	7.19	3.69	0.46	100
	B_{hir}	0.25	12.13	40.5	37.12	2.66	4.08	3.30	100
	B_{ir}	0.04	0.84	2.97	49.80	38.30	7.35	0.69	100
	C	0.02	0.62	12.72	82.4	3.15	1.11	0.03	100.1
Roscommon	A_1	0.23	5.46	16.05	49.20	9.18	16.13	3.87	100.1
	GA_{-1}	0.58	11.50	25.10	54.80	3.55	3.21	0.94	99.7
	GB_{-1}	0.77	13.10	32.80	43.70	4.49	3.75	1.12	99.7
	GA_{-2}	0.17	8.20	33.10	55.40	1.74	1.23	0.43	100.3
	GB_{-2}	0.04	1.50	3.18	53.70	36.75	4.20	0.52	100
	GB_{-3}	0.06	3.27	13.20	69.50	9.40	2.86	1.52	99.8
	C	0.07	16.0	50.0	33.0	0.51	0.57	0.26	100.4

Table 10 Some Physical, Chemical, Mineralogical Characteristics of Kalkaska Sand

Hor-izon	Thick-ness Inches	Vol. Wt. gms/cc	Por-osity	cc/hr Perm-eability	pH	Organic Matter (H_2O_2)	Sol-ution Loss	B.E.C.[1] Meq/gm	Total[2] Surface M^2/gm	Heavy Mineral[3] Content > 2.81 sp.gr.	Feld[3] Spars <2.60 sp.gr.	Quartz[3]
A_1	3"	1.05	60.3	419	5.2	9.56	2.69	1.26	30.5	0.14	7.9	92.1
A_2	10"	1.35	49.1	732	5.1	0.43	0.44	0.29	----	0.10	9.6	90.4
B_{hir}	6"	1.34	49.4	2675	5.6	1.18	2.70	0.64	18.1	0.25	12.9	85.6
B_{ir}	8"	1.36	48.7	2670	5.3	0.87	2.31	0.34	----	0.30	13.1	85.8
C		1.52	42.6	2262	5.5	0.06	1.41	0.17	----	0.29	14.4	86.8

1. Acid insoluble fraction.

2. Before H_2O_2 treatment.

3. Based on heavy liquid studies of the fine sand fraction.

Series and Horizon		Dates														
		1953			1954								1955			
		9-11	11-5	12-14	1-16	3-6	4-10	5-1	6-28	8-20	11-20	12-31	2-19	4-21	6-4	8-10
Kalkaska	A_1	480	570	262	298	297	360	420	432	353	280	242	--	287	390	448
	A_2	617	691	504	659	588	541	628	567	627	219	203	--	217	447	471
	B_{hir}	622	549	511	535	575	458	549	540	509	214	267	--	244	415	393
	B_{ir}	613	658	649	707	746	700	738	646	597	571	275	--	528	415	615
	C	587	699	548	654	642	599	674	629	642	344	319	--	342	401	477
Saugatuck	A_1	514	540	624	664	684	691	711	719	705	437	431	--	552	710	611
	A_2	611	598	531	537	554	563	528	596	556	370	246	--	372	512	422
	B_{hir}	563	587	530	552	555	592	611	688	642	374	266	--	408	549	512
	B_{ir}	247	303	285	228	218	450	438	419	495	355	360	--	360	283	271
Roscommon	A_1	477	585	507	551	434	206	-18	-77	223	-50	-111	-15	-78	-195	249
	GA_1	487	626	433	400	328	-4	-19	-30	433	-1	-37	35	-55	-166	243
	GB_1	462	509	360	374	380	217	166	-17	236	64	26	11	108	-177	254
	GA_2	393	400	309	215	268	106	244	47	19	96	0	46	-65	-121	182
	GB_2	-551	77	82	452	587	342	122	-88	12	74	82	52	102	-86	-226
	C	69	-58	-104	54	102	7	33	38	74	-34	-8	-21	28	-146	59

Table 11 Mean Redox Potentials By Soil Series, Dates and Horizons

Series	Horizon	Q_1	Q_2	Q_3	P_{10}	P_{90}	So	Sk	Ku	Q_2-M
Kalkaska M* = .325	A_1	.460	.290	.223	.780	.082	.696	1.09	5.86	-.035
	A_2	.530	.355	.263	.740	.218	.705	1.05	3.90	.030
	B_{hir}	.450	.335	.270	.660	.230	.775	1.04	4.78	.010
	B_{ir}	.430	.335	.263	.608	.238	.782	1.00	4.40	.010
	C	.390	.305	.263	.525	.230	.820	1.05	2.32	-.020
Saugatuck M = .295	A_1	.385	.26	.105	.630	.042	.522	.78	4.20	-.030
	A_2	.410	.30	.230	.555	.165	.748	1.03	4.33	.005
	B_{hir}	.580	.40	.260	.840	.175	.668	.97	2.08	.105
	B_{ir}	.270	.19	.130	.330	.085	.694	.98	3.50	-.105
	C	.333	.27	.235	.400	.206	.837	1.04	4.08	-.025
Roscommon M = .314	A_1	.350	.237	.130	.580	.041	.609	.90	4.80	-.077
	GA_{-1}	.500	.325	.255	.820	.185	.713	1.09	5.12	.011
	GB_{-1}	.525	.363	.275	.860	.175	.724	1.05	5.48	.049
	GA_{-2}	.480	.345	.275	.690	.230	.756	1.05	2.24	.031
	GB_{-2}	.260	.20	.137	.320	.096	.724	.94	3.62	-.114
	GB_{-3}	.338	.263	.215	.470	.140	.797	1.02	5.32	-.051
	C	.655	.464	.340	.860	.250	.720	1.02	3.86	.150

$$* \quad M = \text{Median} = \frac{\text{Smallest } Q_2 + \text{Largest } Q_2}{2}$$

$$SO = \sqrt{\frac{Q_3}{Q_1}} \qquad Ku = \frac{P_{10} - P_{90}}{\frac{Q_1 - Q_3}{2}}$$

$$Sk = \sqrt{\frac{Q_3 - Q_1}{Q_2}}$$

Table 12 Sorting Analyses for all Horizons of Kalkaska, Saugatuck and Roscommon Series.

Type of Block and Soil Series	Horizon	Inches Depth	Moisture by Dates (Ohms x 1000)* 1-16	3-6	4-10	5-1	6-28	8-20	11-20	12-31
Kalkaska	A_1	5	--	1.59	1.52	1.05	0.97	2.07	--	1.74
	A_2	12	--	1.60	1.56	1.22	1.08	1.54	--	1.74
(Plaster of Paris)	B_{hir}	18	--	1.44	1.50	1.27	1.10	3.65	--	1.88
	B_{ir}	28	--	1.52	1.55	1.36	1.16	1.33	--	340.
	C	44	--	1.56	1.68	1.50	1.27	1.26	1.52	1.70
Saugatuck	A_1	5	120.0	350.0	6.43	4.05	4.70	80.00	2.92	6.75
	A_2	8	84.0	8.55	5.46	4.01	5.00	88.50	3.67	5.20
(Nylon)	B_{hir}	12	79.0	14.1	12.90	9.05	6.71	90.00	5.54	550.0
	B_{ir}	20	64.3	3.99	1.75	6.03	4.15	32.40	3.56	3.90
	C	42	34.5	1.56	1.81	1.29	3.15	7.90	1.26	1.48
Roscommon	A_1	3	6.22	0.84	1.18	0.92	0.97	20.0	1.22	1.58
(Nylon)	GA_{-1}	9	4.40	0.81	1.02	0.87	1.08	21.6	0.99	1.38
	GB_{-1}	15	3.26	1.50	1.95	1.11	1.10	4.20	1.78	2.14
	GA_{-2}	25	0.58	0.97	1.22	1.10	1.16	4.42	1.52	2.06
	C	36	0.56	0.77	1.26	1.06	1.27	1.11	1.11	1.50

* For nylon blocks these readings have approximately the following meaning:

1. Dry = over ten thousand ohms (less than 2% moisture by weight.)
2. Moist = under ten thousand and over twelves hundred ohms (2 - 7% moisture by weight)
3. Wet = less than twelve hundred ohms (saturated with water)

Table 13 Change in Resistance of Bouyoucos Moisture Blocks with Dates in Kalkaska, Saugatuck and Roscommon Sands

Element	Redox Couple	Ec (Volts) at pH 5.0
Iron	$2Fe^{3} + 2Hg + 2Cl^{-} \rightleftharpoons 2Fe^{2} + Hg_2Cl_2$ $2Fe(OH)_2 + 2OH^- + Hg_2Cl_2 \rightleftharpoons Fe(OH)_3 + 2Hg + 2Cl^-$ $2Fe^{2} + 6OH^- + Hg_2Cl_2 \rightleftharpoons Fe(OH)_3 + 2Hg + 2Cl^-$	.526 .274 .080
Manganese	$2Hg + 2Cl^- + MnO_2 + 4H^+ \rightleftharpoons Mn^{2} + 2H_2O + Hg_2Cl_2$	.495
Oxygen	$2Hg + 2Cl^- + \frac{1}{2}O_2 + 2H^+ \rightleftharpoons Hg_2Cl_2 + H_2O$	.689

Table 14 Emf of Spontaneous Oxidation or Reduction Reactions with the Saturated Calomel Electrode at pH 5.0 from Latimer and De Vries

Table 15 Weather Data from Cadillac Weather Station

Month	Date of Redox Determination	Mean Temp. 2 Wks. before Reading	Rainfall (Inches)	Dep. from Normal
September	11	65	3.16	-0.54
October	--	--	1.20	-1.56
November	5	22	1.26	-1.43
December	14	28	1.55	-0.12
January	16	16	2.03	0.33
February	--	--	1.86	0.27
March	6	16	1.62	-0.30
April	10	50	5.13	2.68
May	1	65	3.00	-0.02
June	28	61	7.23	4.13
July	--	--	2.99	0.32
August	20	59	0.65	-2.25
September	--	--	4.27	0.57
October	--	--	6.48	3.72
November	20	35	1.46	-1.23
December	31	23	1.53	-0.14
January	--	--	1.18	-0.52
February	19	28	0.98	-0.61
March	--	--	1.36	0.56
April	21	50	2.01	-0.44
May	--	--	2.44	-0.48
June	4	68	1.67	-1.44
July	--	--	4.63	1.96
August	10	68	1.29	-1.61

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