THE USE OF REDOX POTENTIALS IN STUDIES OF SOIL GENESIS

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THE USE OF REDOX POTENTIALS IN STUDIES OF SOIL GENESIS

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INTRODUCTION

Oxidation and solution are two chemical processes that are involved in the development of the soil body. There is a differential solubility in the oxidized and reduced state of such metallic ions as iron and manganese. For example, ferrous hydroxide is a million times more soluble than ferric hydroxide. This variation in the state of oxidation within the soil body, may be a means whereby such elements are brought into solution, translocated, and precipitated in horizons of different oxidation-reduction status. Therefore a knowledge of the oxidation-reduction potentials in soils may give information usable in explaining soil formation phenomena.

Recently Quispel (29) has described a method whereby the oxidation state of the soil body can be measured *in situ*. An adaptation of his method has been used in this study to measure the oxidation state of the soil body at depths corresponding to key soil horizons and to relate these findings to soil genesis in the podzol region. A laboratory experiment was also performed to see if a redox profile would form in a sand column and what effect this might have on the status of the iron present.

REVIEW OF LITERATURE

Gillespie (10) 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 subjected to waterlogging. This reducing condition was emphasized by the addition of dextrose. The increase in the intensity of the reducing conditions was accompanied by a foul odor. He discussed the significance of reducing conditions and of reduction potentials in soil study. The toxic effect of freshly incorporated green manure may possibly be the result of extreme reduction.

Neller (22), in 1922, found that growing green plants accelerated the oxidation processes in the soil. Using carbon dioxide as the index of the effect of the plants, he found that the average total carbon dioxide recovery from planted cultures was 12.1 percent higher than that from unplanted cultures. Buckwheat, field beans, and soybeans gave respectively 116.5 percent, 70.8 percent, 60.0 percent, increase in carbon dioxide production. He also found that the second crop gave greater increases than the first. All evidence obtained showed that growing plants of buckwheat, field beans, and soybeans had a beneficial effect on the oxidative processes in the substrata in which they were grown and suggested a symbiotic relationship between the soil oxidizing organisms and the growing green plants.

Bouyoucos (2), in 1923, found that different chemical agents have a decidedly different effect on the oxidation of iron both as to rate and extent. The non-oxidizing effect of some reagents may dominate the oxidizing effect of others; and the oxidation can take place even in the absence of oxygen accessible from the air.

In 1932, Willis (39), using Dunbar fine sandy loam, determined the Eh-pH relationship in the soil. He used a special apparatus to provide a nitrogen atmosphere. The soil was treated with lime at rates of from 1/2 ton to four tons per acre. Eh readings and pH measurements were taken and curves prepared. There was an inverse relationship between Eh and pH. Extracts of the limed soils were made and titrated with hydrochloric acid. The same Eh-pH relationship was observed in the extracts, i.e. a decrease in Eh of about sixty millivolts for each unit increase in pH.

In 1934, Bradfield, Batjer, and Oskamp (3) used redox potentials to evaluate soils for orchard purposes. They found that maximum differences occurred in soils in April and May, and that they could eliminate 80 to 90 percent of the poor orchard sites on the basis of redox potentials.

At the same time Brown (4) reviewed the principles involved in the study of soils by means of oxidation-reduction potentials. He stated that by means of data obtained in this way, it may be possible to determine the more exact nature of certain soil processes which are important in plant growth. Brown used a rapid method of measuring Eh in the laboratory, and developed the method of preparing electrodes which were later used by Quispel (29) and Lemon (18).

In the same year Heintze (11) used the glass instead of the calomel electrode as the reference electrode in order to minimize polarization and to facilitate instantaneous Eh-pH measurements. She found that the ratio of soil to water was of little importance in a suspension; and that the presence of air or nitrogen did not affect the potential. She also found that soils, known to contain readily decomposible organic material, on being waterlogged, showed a marked drop in potential as soon as conditions of temperature and pH are favorable; while soils that contained little organic matter tended to resist any drop in Eh. She observed that oxidation-reduction potentials of soils depended so largely on pH that the values should not be considered separately. Highly contrasting soil types with equal pH values gave similar oxidation-reduction potentials. She found that waterlogging brought about a greater change in potential in the Chernozem soils of Russia than in any other soil studied.

In 1935, Kohnke (15) found 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 principle substances entering into the oxidation-reduction reactions of soils are colloidal clay, organic substances and humus, and compounds of iron and manganese. He found the Eh change per unit change in pH to be fifty-nine millivolts in the pH range of two to seven. Colloidal clays showed Eh-pH relationships comparable to those of soils. Aeration increased the oxidation-reduction potential of a soil and waterlogging lowered the potential. The changes took place within two to three days. Seasonal variations in the years 1933-34 were small due to unusually dry weather. Kohnke also found that the oxidation-reduction potentials of surface soils are lower than those of the deeper horizons during the spring. Later on those differences tended to disappear. Quantitative determinations of oxidized and reduced substances in the soil gave large significant differences between well and poorly aerated soils. The experimental error was rather large.

In the same year, Peech and Batjer (24) used 0.1 N sulphuric acid as the suspension medium. They found that the previous use of the electrodes had little effect on the readings and that the suspension was better poised. Some soils appeared to be less susceptible to oxidation in H_2SO_4. They found that no appreciable reduction took place in soils below temperature of 55°F.

In 1936, Sturgis (34) found that low potentials in waterlogged soils were largely caused by the decomposition of fresh organic matter. The solubility of phosphorus was reduced under low potential conditions. In the absence of actively decomposing organic matter, large amounts of iron compounds precipitated on and around the roots of rice plants. Adding gypsum to a waterlogged soil caused the production of sulphides which reduced the yield of rice. The application of leguminous organic matter increased the yield. Sturgis also found that the addition of fresh organic matter to waterlogged soils resulted in potentials as low as eighty millivolts as compared with two hundred millivolts in a waterlogged soil low in organic matter.

At the same time, Darnell and Eisenmenger (8) found that there was little or no change in potential with the addition of fertilizers carrying nitrogen. The changes correlated better with the change in pH. The rapid decomposition of fresh organic matter brought about a marked fall in potential. They explained this fall as being due to oxygen depletion.

Burrows and Cordon (6), in 1936, found that the type of decomposable organic matter in a soil was an important factor in the determination of the reducing intensity that prevailed. They found that the decomposition of casein resulted in highly positive potential levels, while the decomposition of carbohydrate resulted in negative potentials which did not appear to differ greatly from those produced in soil to which organic matter had not been added. They found that moisture did not appreciably affect potentials.

Willis (40) showed that manganese deficiency caused by liming could be explained by consideration of Eh as well as pH. He also stated that the two soil components, organic matter, and oxygen, appeared to govern the oxidation-reduction equilibrium in the soil. Both required activation, the former by micro-organisms, and the latter by catalysis. He further discussed the role of oxidation and reduction in soil fertility, and suggested evidence that phosphorus, potassium, copper, manganese, boron, silicic acid, organic matter, pH, aeration, and temperature are to some degree interdependent variables.

In 1939, Buehrer et al (5) found that the Eh-pH relationship could be determined by simply diluting a soil suspension with water. They showed that the Eh change amounted to about sixty-eight to seventy millivolts per unit change in pH; and they showed that bubbling nitrogen through the soil tended to lower the Eh value. They found that puddling caused a drop in soil Eh which they believed was due to factors other than oxygen depletion, that the presence of abundant oxygen caused an increase in Eh. The addition of alfalfa to a soil suspension caused a marked decrease in Eh, which was taken to be indicative of the nature of the reduced compounds formed during its decomposition.

Stevenson et al (33) working with Oregon soils found that different soil types under field conditions showed little variation in oxidation-reduction potential with the methods used. There was little variation in potential between horizons even when there was a tight subsoil. They also found that fresh organic matter alone in a moist soil did not cause a fall in potential, but waterlogging a wet soil caused a rapid fall in potential. Anaerobic conditions in the soil were not indicated by the oxidation reduction potential in a reliable manner.

Volk (37), working with Alabama soils, did more than anyone to establish a standard technique for the measurement of oxidation-reduction potentials in the laboratory. Batjer, Bradfield, Kohnke, Peech, and Stevenson had all used 0.1 N H_2SO_4 as the suspension medium to inhibit bacterial activity and thus prevent the development of reducing conditions in the soil, and to add poise to the system. Volk claimed that results obtained in this way were not comparable to water suspensions since the sulphuric acid dissolved materials that were not usually active in the soil. Only Kohnke and Willis considered the expulsion of air with nitrogen gas; while Brown, Darnell, Heintze, Sturgis and others disregarded the possibility of a change in potential during the analysis. Volk found that arable soils in a high state of oxidation changed little, but those that were in a reduced state became rapidly oxidized unless air was expelled with nitrogen. He also found that all preservatives used to inhibit bacterial action changed the Eh of the soil. As a substitute for a preservative, Volk cooled all his samples to a point just above freezing. He found this procedure to be effective. Oxidation was prevented by use of water from which the free oxygen was removed by boiling and replaced with nitrogen. All analyses were performed in a nitrogen atmosphere. Volk also found that the Eh-pH relationship was variable between 59 and 101 millivolts for each pH unit. Potential drift was found to be due to the past history of the electrode. Wire electrodes were found to be superior to foil electrodes. He used a battery of thirty glass electrodes and 120 blank electrodes and was able to run fifteen to twenty samples per hour.

Also, about the same time, Volk (35) made extensive studies of Alabama soils. He found that cultivated soils, in general, had a higher Eh value than did virgin soils in the zero to eight inch depth; but there was little difference in the subsoils. He found that differences resulting from soil type variations rarely exceeded fifty millivolts. These he did not think important since they could have been due to differences in soil material rather than to state of oxidation. Swampy soils, for example, frequently had higher Eh values than did well drained upland soils. After a rain the Eh rose for a time which Volk explained by suggesting that the rainwater carried oxygen into the soil. When the excess oxygen was removed and conditions were once again stable, the Eh of the soil returned to normal. Seasonal variations in Alabama soils did not exceed sixty millivolts. Volk does not think that Eh is an indicater of the oxidation state of the soil since it is dependent, not only on the relative amounts and kinds of the ions present but also on the ratio of oxidized to reduced substances present. In another paper in 1939 (36), Volk made a study of the effect of Eh on the growth of plants. He controlled conditions so that no other factor was limiting, and was able to adjust the Eh of the nutrient solution from 525 to 325 millivolts by use of hydroquinone. The hydroquinone had no toxic effect on young seedlings in concentrations up to fifteen ppm. and in later stages of growth, he could use concentrations up to sixty to seventy ppm. There was no limiting effect of Eh on plants in the range of 325 to 525 millivolts. He concluded that Eh was not limiting to plant growth on Alabama soils.

Keaton and Kardos (14), in 1940, concluded that the oxidative character of the soil was reflected in the redox potential. Because of the complexity of the soil medium, however, they did not consider potential to be that of an individual system; but regarded it as the function of many complex interlocking systems. With this in mind, they suggested that redox potential may be used in the study and interpretation of the general chemical processes taking place in the soil. They studied the effect of various materials on the arsenite-arsenate system. They were able to show that ferric oxide raised the potential and caused arsenite to be oxidized to arsenate. Alumina produced no effect on the system. Clay colloids tended to shift the equilibrium in the opposite direction, i.e., arsenate was reduced to arsenite; and at the same time the potential was lowered. Their interpretations were based on calculations using the Nernst equation. They further concluded that the addition of iron in the oxidized form caused increases in plant growth in soils poisoned with arsenical spray residues; and that the beneficial effect was primarily due to increased fixation of arsenate as it was oxidized from arsenite to arsenate.

The next significant advance occured in 1947 when Quispel (29) measured redox potentials <u>in situ</u>. 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 <u>in situ</u>, Quispel recommended that a great many readings be taken. He found that oxygen also affected the potential greatly; thus the Eh of the soil was determined in part by the state of aeration of the soil. When the potential of a soil was determined in the field, it was possible to define the aerobic or anaerobic character of the soil in terms of Eh.

In the same year Roberts (30) working with micro-organisms found that B. 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 great number of cultures isolated from the soil and he found that only B. polymyxa and one culture of Clostridium sp. reduced iron in appreciable amounts. These were facultative aerobic bacilli.

Bertramson and White (1) give an excellent review of the literature dealing with oxidation-reduction potentials in recent years. They concluded that the Eh 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 therefore varied from soil to soil. They were critical of present laboratory techniques since there are no suitable methods for measuring Eh in the soil in a manner similar to the measurement of pH. According to them the present field quick test for ferrous iron may be more suitable for the measurement of reducing conditions in the soil.

In 1949, LaFonde (16) investigated 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 strong acidity. La Fonde concluded that redox potentials could be used to characterize forest humus types.

In the same year, Wilde and others (38) 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 1950, Pierce (26) 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 1953, Pierce (25) measured pH, specific conductance and redox potentials in situ in swamps supporting different types of forest vegetation. There was a close correlation between redox potential and the oxygen content of the ground water and with the rate of tree growth. The specific conductance, a measure of the electrolyte content, was found to influence the forest type rather than the rate of growth. These studies were carried out in Wisconsin. Further studies in the Hearst region of Ontario gave similar results.

From the literature it is apparent that the measurement of the redox potential of the soil has been hampered in the past by lack of consideration of all the factors involved. From the scattered studies of the nature of these factors it is suggested that their normal effect on the soil can best be studied in the field, or if laboratory studies are carried out, field conditions should be similated as closely as possible. The redox potential of the soil appears to be tied up very closely with the oxygen content; and also with some of the materials within the soil such as iron, organic matter and manganese. There may also be other materials involved. Plants seem to indicate that a deficiency of oxygen exists in the soil before the deficiency can be observed through change in the redox potential. This is true because the redox system in the soil is more or less well poised or buffered. Nevertheless, the study of the redox system in the soil may be useful in the study of soil genesis since those factors that determine the redox state are also important in soil genesis.

THEORETICAL CONSIDERATIONS

Redox Potentials

When a metal is placed in contact with a solution of its ions, it acquires a charge; and if two such electrodes are connected to form a cell, a current will flow which is an expression of the difference in potential between the two electrodes. The positive cell becomes reduced, and the negative one becomes oxidized. Thus, where ever oxidation is taking place, reduction is also taking place. The system is spoken of as an oxidation-reduction system. In this paper the contraction, redox, is therefore used to replace the longer term, oxidation-reduction.

When a cell is reversible, it is possible to relate the electrical phenomena observed to the chemical activity taking place by means of the Nernst equation.

$$Eh = Eo -/- \frac{RT}{nF} Log \left(\frac{Ox}{Red}\right)$$

To date, no one has been able to establish the actual value of a half cell in volts; but two half cells together have a potential which can be measured. When one of the half cells such as the hydrogen electrode or the calomel electrode is selected as a standard all cells can be given definite relative values. The Eh value is taken as the potential difference between two half cells when they have been connected. From the Nernst equation, it is evident that when $\frac{(Ox)}{(Red)} = 1$, then Eh = Eo. This makes it possible to express relative oxidation-reduction intensities in terms of electrode potentials.

It should be made clear that redox potentials are not a measure of the amount of oxidation or reduction that takes place. They are a measure of the oxidizing or reducing intensity or tendency. This is quite a different matter from the capacity of a system to oxidize or reduce. Some idea of the capacity of a system to oxidize or reduce can be obtained by titration with a strong oxidizing or reducing agent.

Eo can be determined for a system. It represents the potential at fifty percent oxidation and fifty percent reduction of the system; and depending on the flatness of the Eh curve as the system becomes relatively more oxidized or reduced the system will be well or poorly poised. If a system is well poised at a certain Eo value, it will tend to be oxidized by any other such system that has a higher Eo value; and it will tend to be reduced by any other such system that has a lower Eo value. Therefore redox potentials can be plotted on a scale and compared in their ability to oxidize or reduce other systems.

Another important consideration is that any particular system can be measured if it is reversible and the Nernst equation is applicable to that system.

This theory has been thoroughly discussed in a collection of reprints published by the United States Public Health Service (7). Figure 1. shows a number of theoretical curves of Eh values which indicate the variation of Eh with the relative percentage of oxidation and reduction and how the different systems can be compared. Note that the steep curve is the most poorly poised. When the soil is considered

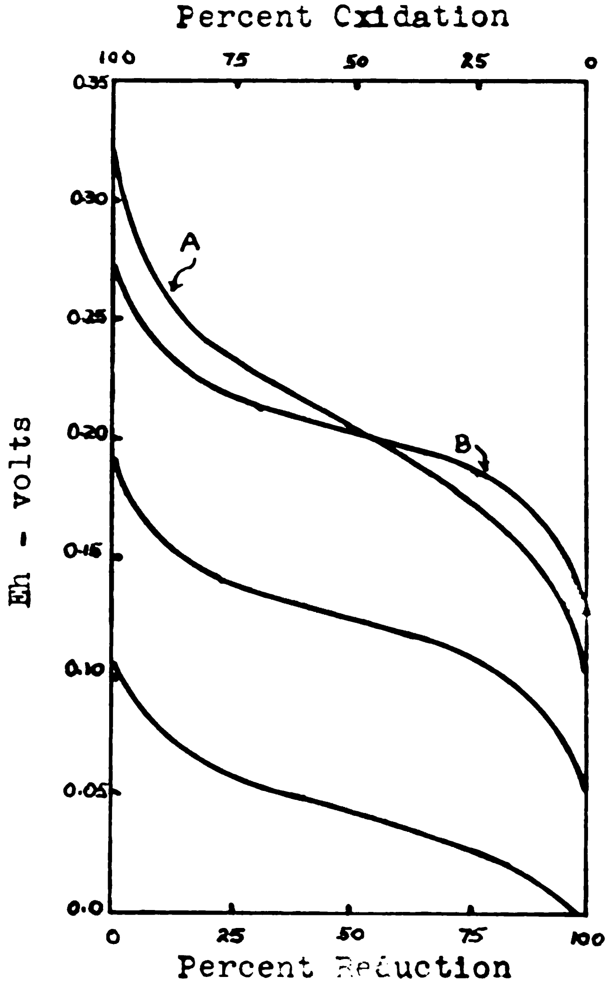

Figure 1. The relationship between Eh and the relative amount of oxidation or reduction for several theoretical systems.

as a natural dynamic system, it is inferred that some of the processes involved in soil development may be redox precesses. If such is the case, then the Eh of the soil will be indicative of the overall state of oxidation of the soil.

Factors Affecting Redox Potentials of Soils

Since Gillespie's time much work has been done; and apart from the contribution made in the field of oxidation and reduction in biology, a number of factors which affect redox potentials in the soil have been observed. These may be considered to be of three main types. First, there are the environmental factors, climate, aeration, and soil disturbances such as cultivation and compaction. Second, there are factors active in the soil medium such as mineral elements, clay colloids, organic matter, micro-organisms and growing plants. Third, there are variations in the redox potential which are caused by the treatment of the soil prior to the measurement of the potential and by the method used in obtaining the measurement.

Volk found that reduced soils quickly become oxidized when they are exposed to the air. For this reason he placed his samples in nitrogen saturated water and froze them before storage for analysis. Other investigators placed the samples in water and allowed them to stand for a number of hours before measuring the redox potential. Some have used sulphuric acid instead of water as the medium for their measurements. In all cases the relationship between the soil sample and its environment is destroyed and the results obtained are not representative of the true oxidative state of the soil. It is maintained that a much more representative picture of the oxidation state of the soil can be obtained by measuring the redox potentials of the soil <u>in situ</u> as some investigators have done (16, 25, 29, 38). All investigators except Quispel and those who followed him have neglected to consider this point.

Significance of Eh

From the discussion above, it can be seen that the factors affecting the redox potential or Eh of the soil are numerous and varied. Because of the complexity in the soil medium, the oxidation-reduction system should be regarded as a number of individual systems operating simultaneously. The redox potential of the soil is a measure of the oxidation-reduction status of all the component systems. Variations in any one of such factors as degree of aeration, moisture content, temperature, microbial population, or stage of decomposition of organic matter will cause changes in the oxidation state of the soil and will be reflected in the redox potential. Such factors are also considered among the factors of soil formation (12). On this basis, the redox system in the soil may be considered as related to soil genesis. The measurement of redox potentials may therefore serve as a useful tool in the study of soil forming processes.

The Podzolization Process

In general, Podzolization is the group of soil formation processes that result in development of Podzol soils. This involves the leaching of bases and translocation of sesqui-oxides and organic matter from the A to the B horizon. In the B horizon the sesqui-oxides and organic matter are deposited, often in layers with the organic matter above, but often in one layer with the sesqui-oxides and organic matter intimately mixed.

Morphologically speaking, the profile produced is very striking. The gray, ashy A_2 horizon, sometimes called bleicherde, contrasts greatly with the reddish brown to dark brown ortstein or orterde B horizon. The overlying A_1 horizon may be lacking, in which case, the Ao and Aoo horizons make up the surface layers. There is then a very sharp boundary between the surface horizons and the underlying A_2 horizon. This may indicate a very complete conversion of organic matter into materials which become mobile in the A_0 and A_1 horizons and are transported through the A_2 horizon into the B horizon where precipitation takes place. Not all materials are precipitated in the B horizon however (13, 31). Puustjarvi et al (28), in Sweden, noted the accumulation of rust precipitates in drainage lines and ditches. This trouble occured in recently glaciated areas. Joffe (13) noted the aluminum in the drainage waters of New Jersey streams.

A most commonly accepted theory of podzolization is that the sesqui-oxides and organic matter are translocated in the colloidal state, and precipitated in the B horizon due to the presence of electrolyte. In Europe, Dr. Albert found a relationship between the depth of penetration of summer rains and depth to the B horizon or ortstein. He also investigated the possibility of the oxides being precipitated by oxygen in the B horizon, and found neither a deficiency of oxygen in the A horizon nor any excess in the B horizon. He concluded that oxygen played little part in the development of the profile. In Sweden, Aarnio conducted laboratory experiments in connection with the precipitation of oxides and organic matter in the B horizon. He was able to show that organic matter and iron in colloidal solution could be precipitated due to mutual effects at certain concentrations. In addition to the iron oxides and organic matter, manganese and phosphorus are deposited in the B horizon.

An excellent discussion of these works and their importance is given in lectures by Marbut (79).

Most theories on podzolization are connected with organic matter in some manner. This serves to indicate the importance of organic matter in the process. Podzols occur in a cool humid climate, and are commonly found in Michigan under hardwood or coniferous types of vegetation, although they may occur under a grass type as well. Podzols also develop on a variety of parent materials ranging from alkaline to acid in reaction and from sands to loams or finer textured materials.

There seems to be no doubt that organic matter and its decomposition products play a very important part in the podzolization process as do iron, aluminum, and manganese. Organic matter and its decomposition products have been shown to be effective in lowering the redox potential of soils (29). Iron and manganese also play an important part in the oxidation-reduction processes that operate in the soil medium, and there are also other mineral elements that could play a part as well. Therefore it is logical to expect that oxidation and reduction may also play an important part in the development of podzols. Since podzols have been shown to form in a relatively short time, they offer possibilities for redox studies in relation to soil development.

THE FIELD EXPERIMENT

For the field experiment, two sites were selected in Sanilac County, Michigan. They showed development of the podzol type profile commonly found in the transition zone between the Podzol region in northern Michigan and the Gray Brown Podzolic region in southern Michigan. A discussion of these soils may be found in a publication by Gardner and Whiteside (9). The soils at both sites developed on glacial drift of Cary Age. McBride fine sandy loam is a well drained soil developed on sandy loam parent material. Marlette loam is another well drained soil developed on loam parent material. A third soil, Parkhill loam, is a poorly drained soil, which occurred in association with Marlette loam. It also is developed on loam parent material. The selection of these soils permitted the comparison of soils that differed in both texture and drainage. The following profile descriptions are of these soils.

McBride Fine Sandy Loam

Location:	T 12 N - R 13 E Section 27, SE¼, of the NE¼, Sanilac County, Michigan.
Vegetative cover:	The present cover consists of a mixture of White Birch (Betula papyrifera), and Trembling Aspen, (Populus tremuloides). The original cover was White Pine (Pinus strobus), and Hemlock (Tsuga canadensis).

Physiography: Rolling till plain of Cary Age at the western edge of the Whittlesey lake bed in Sanilac County, Michigan.

Slope: Six percent.

Profile:

Horizon	Depth	Description
Ao, Aoo	1-0"	Leaf litter and partially decomposed organic matter black in color.
A_1	0-1"	Dark grayish yellowish brown, (10 YR 2/2)*, fine sandy loam with a crumb structure, high in organic matter, friable when moist, pH 5.3.
A_{2P}	1-3"	Light yellowish brown (10 YR 7/3), loamy sand, weak crumb structure, pH 5.3.
B_{2P}	3-9"	Strong yellowish brown (7.5 YR 5/6), loam, crumb structure, friable when moist, pH 4.5.
A_{2GB}	9-15"	Light yellowish brown (10 YR 6/3), sandy loam, weak platy structure, friable, pH 5.2.
B_{2GB}	15-48"	Moderate yellowish brown (10 YR 5/4), silt loam, weak blocky structure, friable when moist, pH 5.1.
C_1	48-72"	Light yellowish brown (10 YR 6/4), silt, massive, friable when moist, pH 5.0.
C	72"	Light yellowish brown (10 YR 6/4), silt, stone free glacial drift, pH 6.5.

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* Munsell color notation. and ISCC - NBS color names.

Marlette Loam

Location:	T 11 N - R 12 E Section 30 NW¼ of NE¼, Sanilac County, Michigan.
Vegetation:	The present cover is American Elm (Ulmus americana), and White Birch. The original cover was sugar maple, elm, hemlock, and birch.
Physiography:	The site is located at the western extremity of the Yale moraine, of Cary age.
Slope:	Six percent.

Profile:

Horizon	Depth	Description
A_1	0-3"	Brownish gray (10 YR 4/1), loam, fine granular structure, friable when moist, pH 6.0.
A_{2P}	3-6"	Light grayish yellowish brown (10 YR 6/2), loam, fine granular structure, friable when moist, pH 5.0.
B_{2P}	6-11"	Moderate yellowish brown (10 YR 5/4), loam, fine granular structure, friable when moist, pH 5.0.
A_{2GB}	11-15"	Grayish yellowish brown (10 YR 5/3), light clay loam, weak medium angular blocky structure, sticky when wet, pH 5.2.
B_{2GB}	15-30"	Moderate yellowish brown (10 YR 4/4), clay loam, plastic when wet, pH 6.8, medium to coarse angular blocky structure.
C	30"	Grayish yellowish brown (10 YR 5/2), light clay loam, with dark grayish (10 YR 4/2) mottles, medium to coarse angular blocky structure, glacial till, calcareous.

Parkhill Loam

Location:	T 11 N - R 12 E Section 30 NW¼ of NE¼, Sanilac County, Michigan.
Vegetation:	The present cover is American Elm, and White Birch. The original cover was sugar maple, elm, hemlock, and birch.
Physiography:	The site is located at the western extremity of the Yale moraine, of Cary age.
Slope:	Level to depressional.

Profile:

Horizon	Depth	Description
A_1	0-6"	Brownish black (10 YR 2/1), loam, fine granular structure, friable when moist, pH 6.5.
A_G	6-10"	Light grayish yellowish brown (10 YR 6/2), light loam, weak fine angular blocky structure, friable when moist, pH 6.5.
B_G	10-16"	Grayish yellowish brown (10 YR 5/2), clay loam with light yellowish brown (10 YR 6/4) mottles, medium angular blocky structure, sticky when wet, pH 6.5.
G_{B3}	16-42"	Light grayish yellowish brown (10 YR 6/2), mottled, medium angular blocky structure, mottled brownish yellow, light clay loam, sticky when wet, pH 7.5.
C_1	42"	Light grayish yellowish brown (10 YR 6/2), mottled light yellowish brown (10 YR 6/4), loam to light clay loam till, pH 7.8.

Installation of Electrodes

Electrodes, prepared in the manner described by Guispel (29), were installed in groups. Copper connections were made of different lengths so that the electrodes could be installed at the selected depths. The most suitable time for installation of the electrodes was in early spring after the frost was gone but while the soil was still saturated. At that time there was little difficulty in forcing the electrodes into the soil and little breakage occurred. After the soil became dry the electrodes were checked to make sure that the soil had not shrunk away to allow an excess of air to enter the soil.

After a general examination of each site to select a suitable profile, three auger holes were made three feet apart in a triangular pattern as shown in Figure 2. The depth and thickness of each horizon in the profile was measured. Holes were then punched in the wet soil within the triangle to the required depth with a sharpened steel rod.

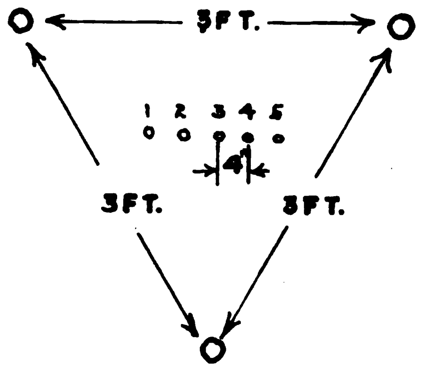


Figure 2. Layout of Electrodes <u>in situ</u>.

The probe was selected of a diameter slightly smaller than the electrodes to insure a tight fit and thus prevent the passage of excess air to the electrode. Electrodes of the proper length to reach the desired soil horizon were then forced carefully into the soil through the holes made with the probe.

Three sets of electrodes were installed in the Marlette loam at the Kenneth Knight site and two sets were installed in McBride fine sandy loam at the Dan Jurn site. Each of these sets consisted of five electrodes. An additional two sets consisting of three electrodes each were installed in the Parkhill loam at the Kenneth Knight site.

Measurement of Redox Potentials

The electrodes were installed in the latter part of April and readings with a Beckman vacuum tube potentiometer were taken weekly during the first month. Later they were taken only monthly. The saturated calomel electrode served as the standard, or reference electrode. The cell was as follows:

Pt / HgCl, KCl // Soil / Pt

The KCl bridge was formed by wetting the soil with a saturated KCl solution, and inserting the calomel electrode a few inches into the soil. The potentiometer could then be connected to the calomel and platinum electrodes, and the reading taken. Polarization of the platinum electrode was prevented by making an approximate adjustment of the potentiometer before completing the connection. Then only small corrections were required to get the reading and a minimum of current flow took place. Several precautions were necessary to insure satisfactory readings. The electrode leads had to be perfectly dry to prevent shorting of the circuit when the connection was made. The most suitable time for taking readings was in the early afternoon. The readings were easily affected by plants in close proximity, If the plant stems touched the leads they affected the readings. In the early spring when the soil was saturated and there was a breeze, the trees rocked; and the roots in the vicinity of the electrode disturbed the soil enough to cause very unsteady readings. At the same time when the soil was saturated, the soil solution was very dilute and therefore poorly poised. This resulted in some very unsteady readings. Later when the soil was drier, the readings were quite stable and reproducible.

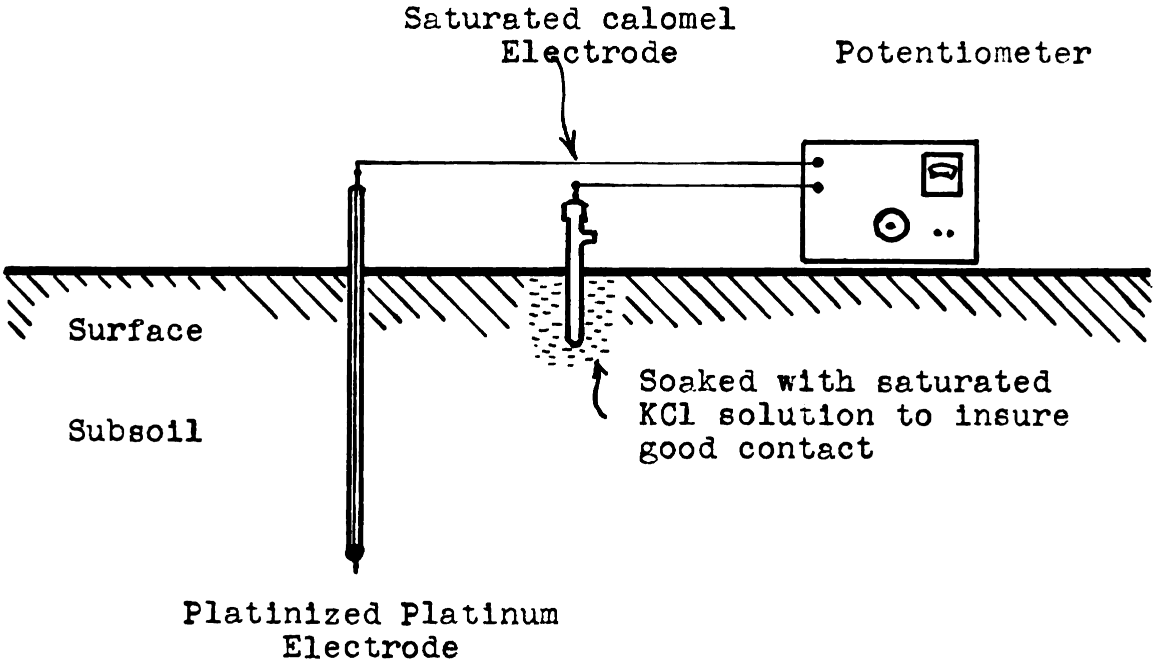


Figure 3. Method of making redox measurements *in situ*.

The electrodes were set out on the 25th of April and readings taken regularly until the 10th of November. The electrode sets at the Dan Jurn site were then dug out, profile descriptions taken, and samples collected for laboratory analysis. In November the weather was too cold for working out of doors. The Beckman pH meter would not function properly below 10°C, and samples for pH measurement had to be taken to a warm place before pH readings could be taken. Due to these difficulties the remaining electrode sets were left in the soil over winter to observe what occurred. Little change was observed during the early part of the winter; and considerable difficulty was experienced getting readings through the snow. Frost heaved the electrodes; and they had to be reset a number of times. Moisture shorted out the readings, and great care was required to get readings. Special equipment is needed to measure redox potentials during winter weather; and to prevent heaving of the electrodes by the frost.

Figures 4, 5, 6 show the data for McBride fine sandy loam, Marlette loam and Parkhill loam. All results were corrected to pH 5.0 to make them comparable and at the same time to represent the natural soil condition as closely as possible.

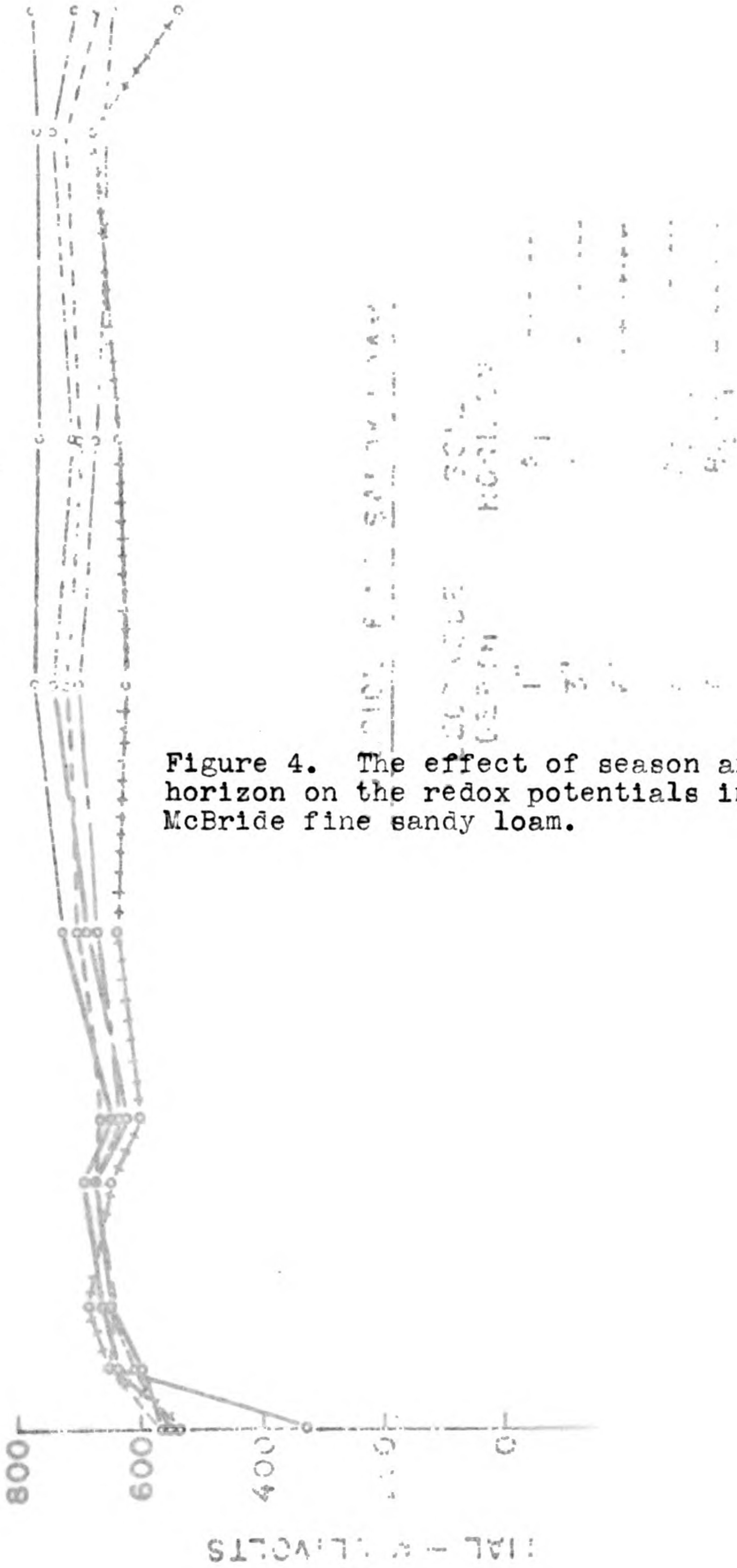
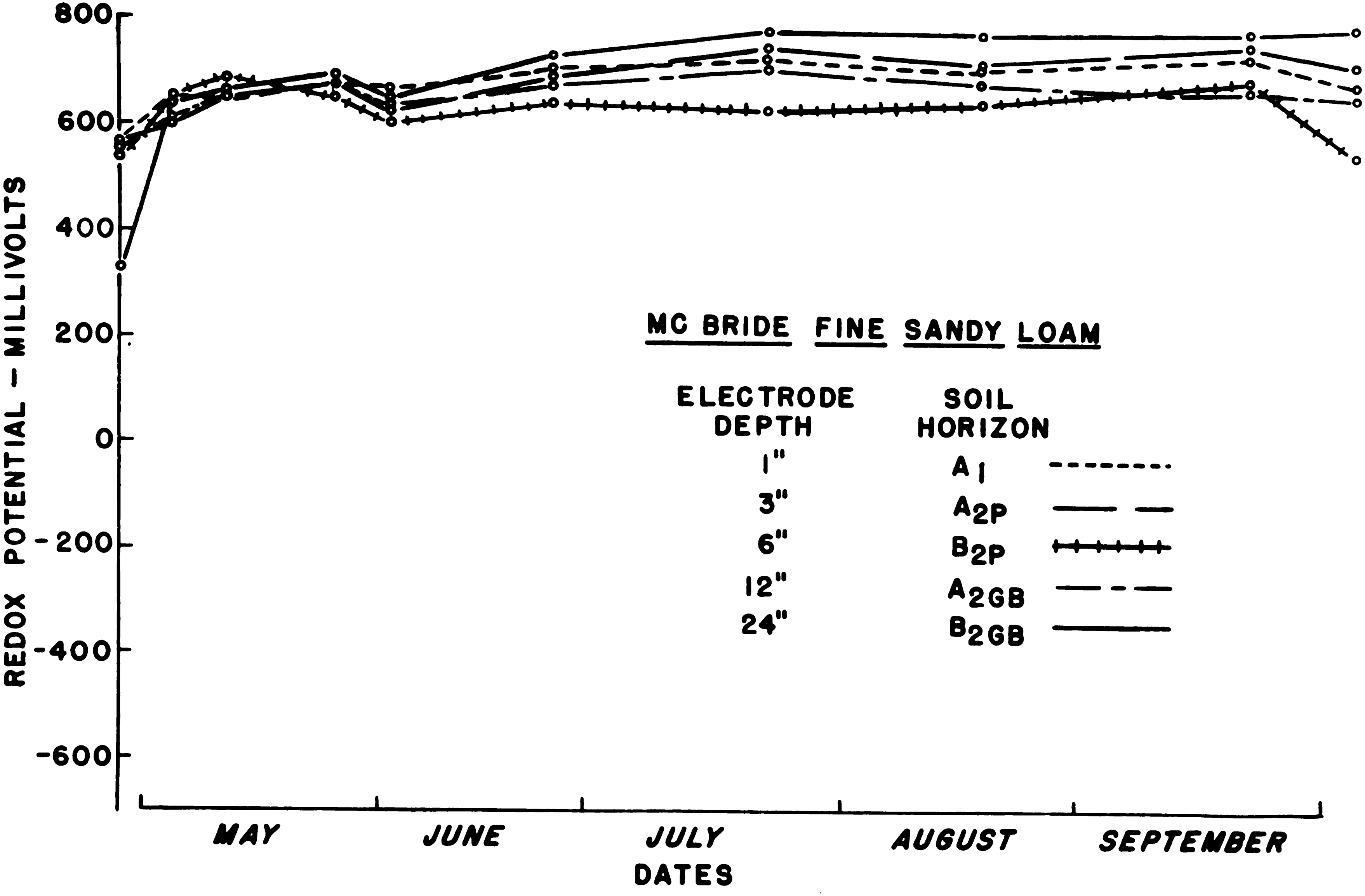


Figure 4. The effect of season and horizon on the redox potentials in McBride fine sandy loam.


800
600
400
200
0
-200
-400
-600
REDOX POTENTIAL - MILLIVOLTS
MAY
JUNE
JULY
AUGUST
SEPTEMBER
DATES
MC BRIDE FINE SANDY LOAM
ELECTRODE DEPTH
SOIL HORIZON
1" A1
3" A2P
6" B2P
12" A2GB
24" B2GB

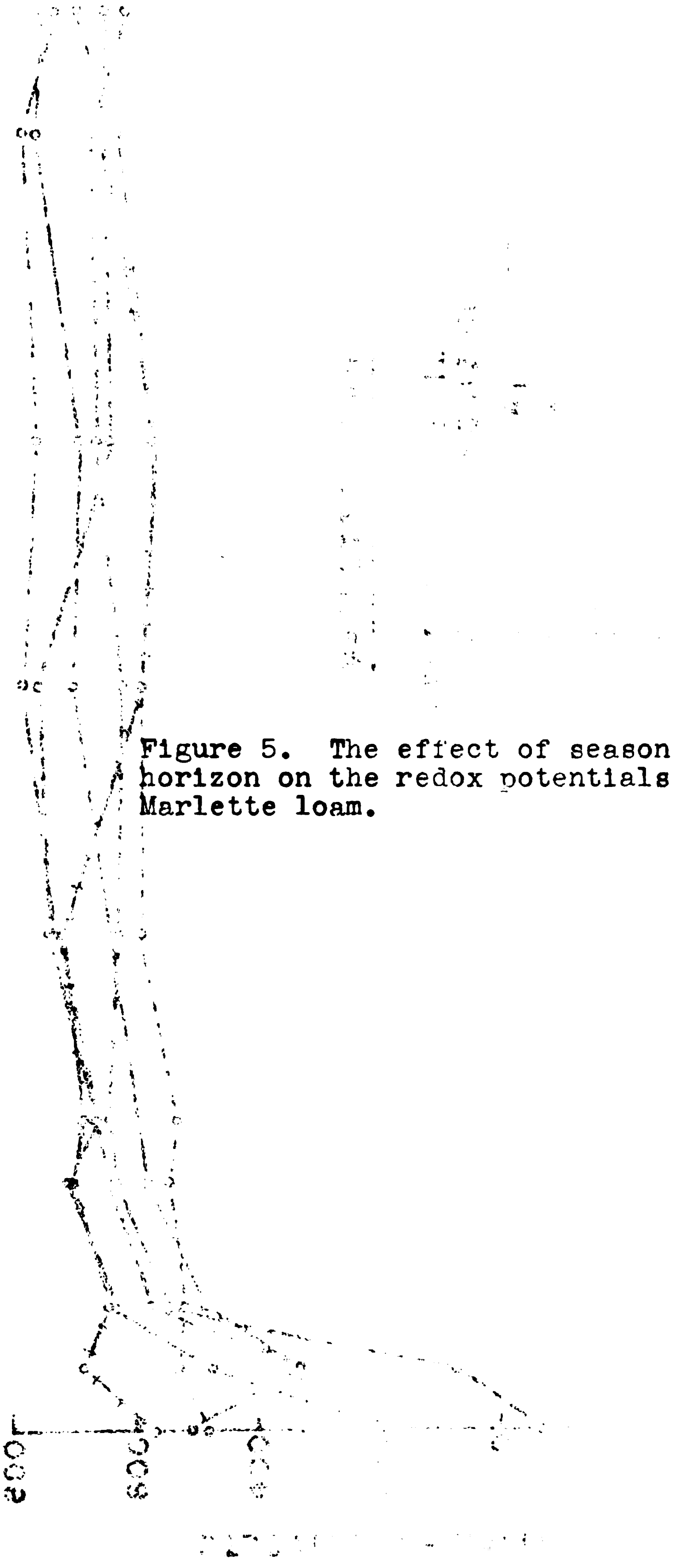
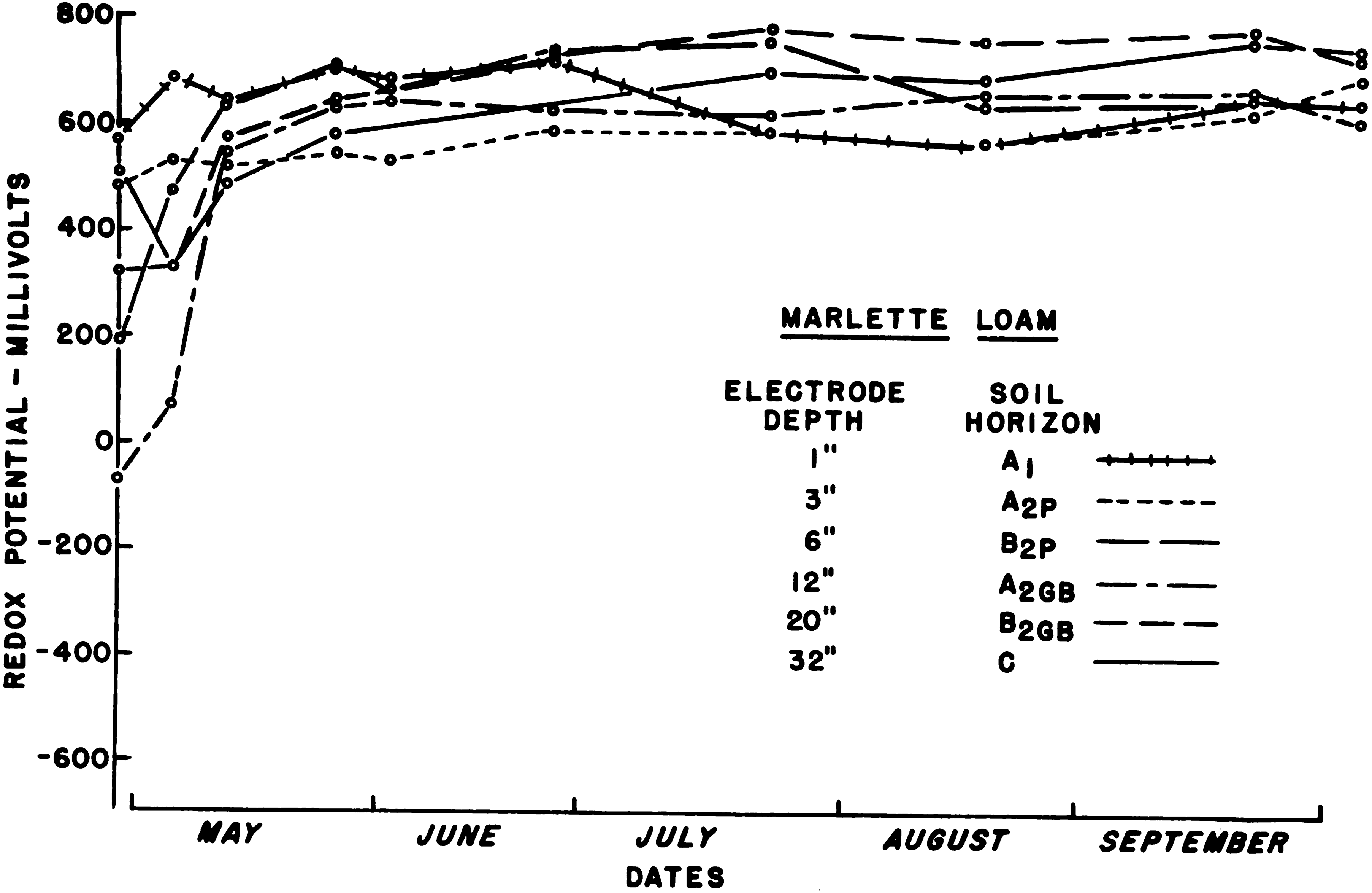


Figure 5. The effect of season and horizon on the redox potentials in Marlette loam.


800
600
400
200
0
-200
-400
-600
REDOX POTENTIAL - MILLIVOLTS
MAY
JUNE
JULY
AUGUST
SEPTEMBER
DATES
MARLETTE LOAM
ELECTRODE DEPTH
SOIL HORIZON
1" A1
3" A2P
6" B2P
12" A2GB
20" B2GB
32" C

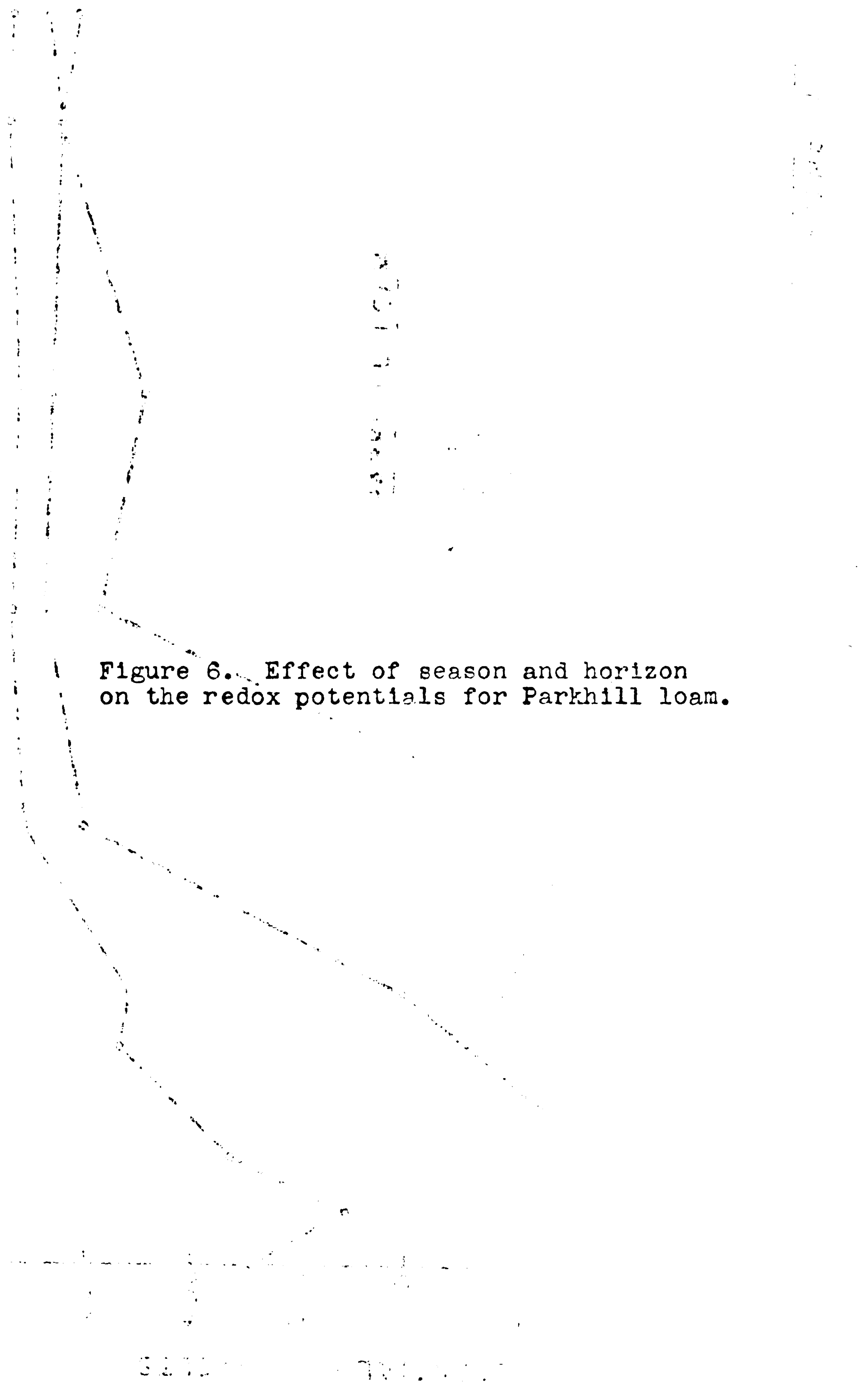
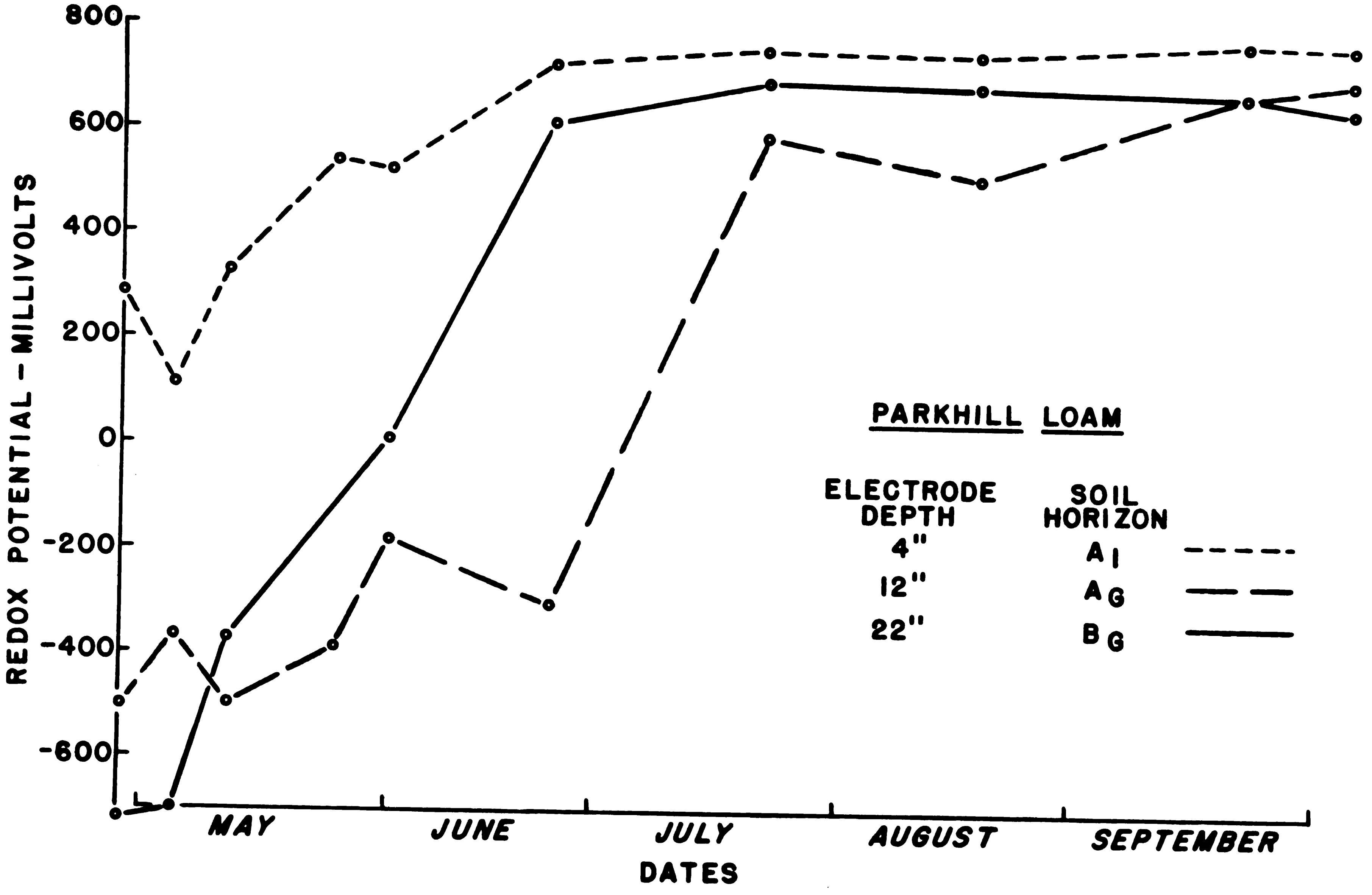


Figure 6. Effect of season and horizon on the redox potentials for Parkhill loam.


PARKHILL LOAM
ELECTRODE DEPTH
SOIL HORIZON
4" A_1
12" A_G
22" B_G
800
600
400
200
0
-200
-400
-600
REDOX POTENTIAL - MILLIVOLTS
MAY
JUNE
JULY
AUGUST
SEPTEMBER
DATES

LABORATORY EXPERIMENTS

The Eh-pH Relationship

The data collected in the field could not be considered comparable until it had been corrected for pH. A modification of Willis' method (39) was used to determine the Eh-pH relationship. The apparatus, shown in Figure 7, was set up as follows: a glass electrode, a calomel electrode and two platinum electrodes were fitted tightly for support into a large rubber stopper which would fit a heavy glass tumbler.

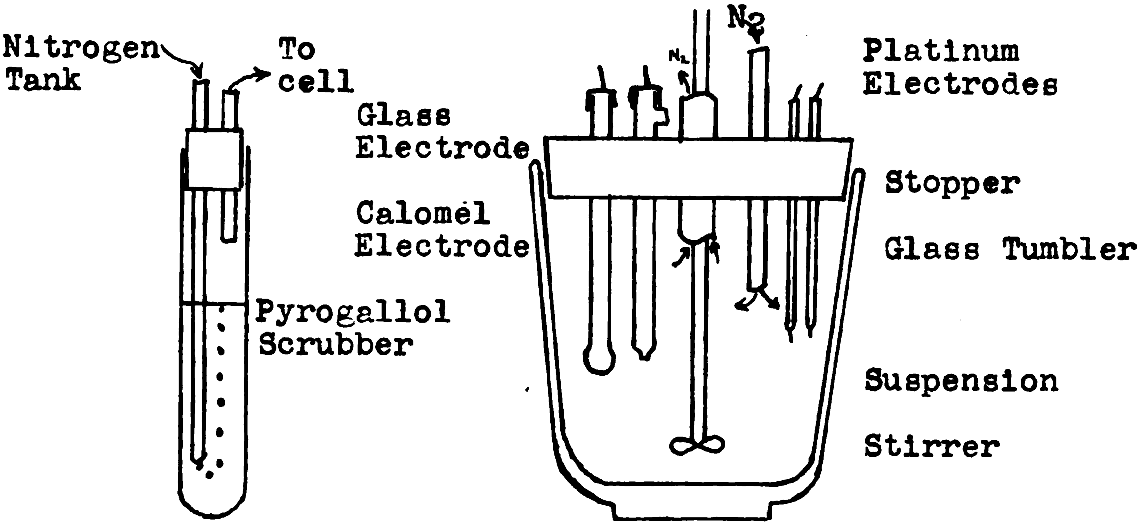


Figure 7. Nitrogen cell for measuring Eh-pH relationships.

Inlet and outlet holes for nitrogen gas were also cut in the stopper. A glass stirring rod was fitted into the center of the stopper through a glass sleeve and adjusted so that it could be rotated with an electric motor. Nitrogen gas was introduced through a small glass tube so that it was distributed over the surface of the soil suspension and the air was excluded. The nitrogen gas used was first conducted through an alkaline pyrogallol scrubber to remove all traces of oxygen. Boiled water was used for preparation of the soil suspensions. A 1:1 suspension could be used and this made it possible to measure both Eh and pH at the same time. The pH values of the soil suspension were varied by the addition of different amounts of 0.1 N sulphuric acid and 0.1 normal sodium hydroxide. The sample was stirred for five minutes and the Eh measured as soon as the streaming potential had subsided and the reading became steady. The pH was measured at the same time. Beckman equipment was used for both Eh and pH measurements.

In Figure 1 of the appendix it can be seen that there is a straight line relationship between Eh and pH. This agrees with the findings of Willis (39). However, results also indicate that the theoretical values of fifty-nine millivolts is not a constant for all soils but may be a value which is characteristic for each soil. This result agrees with the findings of Volk (33). There was not a significant difference between values for the individual horizons in this case. Therefore the Eh-pH relationship should be determined for each soil studied.

Using these data, all horizons were corrected to pH 5.0 in order to make the readings most representative of the natural soil condition. For the Dan Jurn Site this required the least amount of correction. For the Kenneth Knight Site the samples were not taken until the following summer. For this reason, Willis' theoretical value of 59 millivolts was used to correct the readings for the Marlette and the Parkhill loams.

The Laboratory Experiment

All results obtained in the field were extremely variable. Therefore, there was a large experimental error. For this reason, it was decided to set up a laboratory experiment to try and control some of the variables in such a way as to reduce some of the variability and still simulate natural field conditions as closely as possible. Enough replicates were used so that the data could be analyzed statistically for significance. By this method, it was hoped that the experimental error could be evaluated. For this experiment, a sample of the C_1 horizon taken from a Weare sand profile on an old horse shoe dune in Sanilac County was used. At the same time, a sample of an A_0, A_1 mixture was obtained. The profile description follows:

Weare Sand

Location: T 13 N - R 13 E Section 22 SW¼ of the NW¼ Sanilac County, Michigan. The site is located 1¼ miles south of the village of Argyle on the east side of M-19.

Vegetation: The site supported a moderately dense cover of Trembling Aspen with a ground cover of Wintergreen and Bracken.

Physiographic position: The site was located on an old sand dune in the interlobate region of the Thumb region of Michigan.

Profile:

A_1	0-5 inches	Grayish brown (7.5 YR 3/2), loamy sand, high in organic matter, pH 5.0.
A_2	5-12 inches	Grayish yellowish pink (7.5 YR 7/2), sand, pH 4.5.
B_2	12-30 inches	Strong yellowish brown (7.5 YR 5/6), loamy sand, discontinuous ortstein, pH 4.5.
C_1	30 inches	Light yellowish brown (10 YR 7/6), sand, pH 5.0.

A large sample was collected from the C_1 horizon and allowed to dry. The sample was then thoroughly mixed to eliminate variability of the material and to get a reasonably homogeneous sample particularly with respect to pH. This eliminated the need for determination of the Eh-pH relationship. At the same time a sample of the A_0 and A_1 horizon was taken, dried, and thoroughly mixed. Using these materials, the following experiment was performed to simulate, as closely as possible, natural field conditions.

A tension table was constructed using the purest obtainable plaster of paris with an arrangement of glass beakers for adjustment of the water tension. A cylinder of three inch metal downspouting twenty-four inches long was painted on the inside with Tygon paint, placed on the tension table and supported by a ring stand. The joint between the table and cylinder was sealed with wax to make it water tight. The cylinder was then filled with the sand from the Weare sample to within three inches of the top, and four platinized platinum electrodes prepared as in the field experiment were placed in the sand at selected depths for redox measurements. An additional four shiny platinum electrodes were placed at the same depths, and used to measure oxygen diffusion according to the method of Lemon (18). The cylinders were then filled with about 2½ inches of the Ao, A_1 mixture. Two methods of watering were then compared, with each treatment replicated five times. A third treatment, also replicated five times, provided for only enough water to moisten the organic layer. Due to difficulties encountered with this treatment it was discontinued and the results are not shown. The apparatus for a single sand column and the entire green house set-up are shown in Figures 8 and 9.

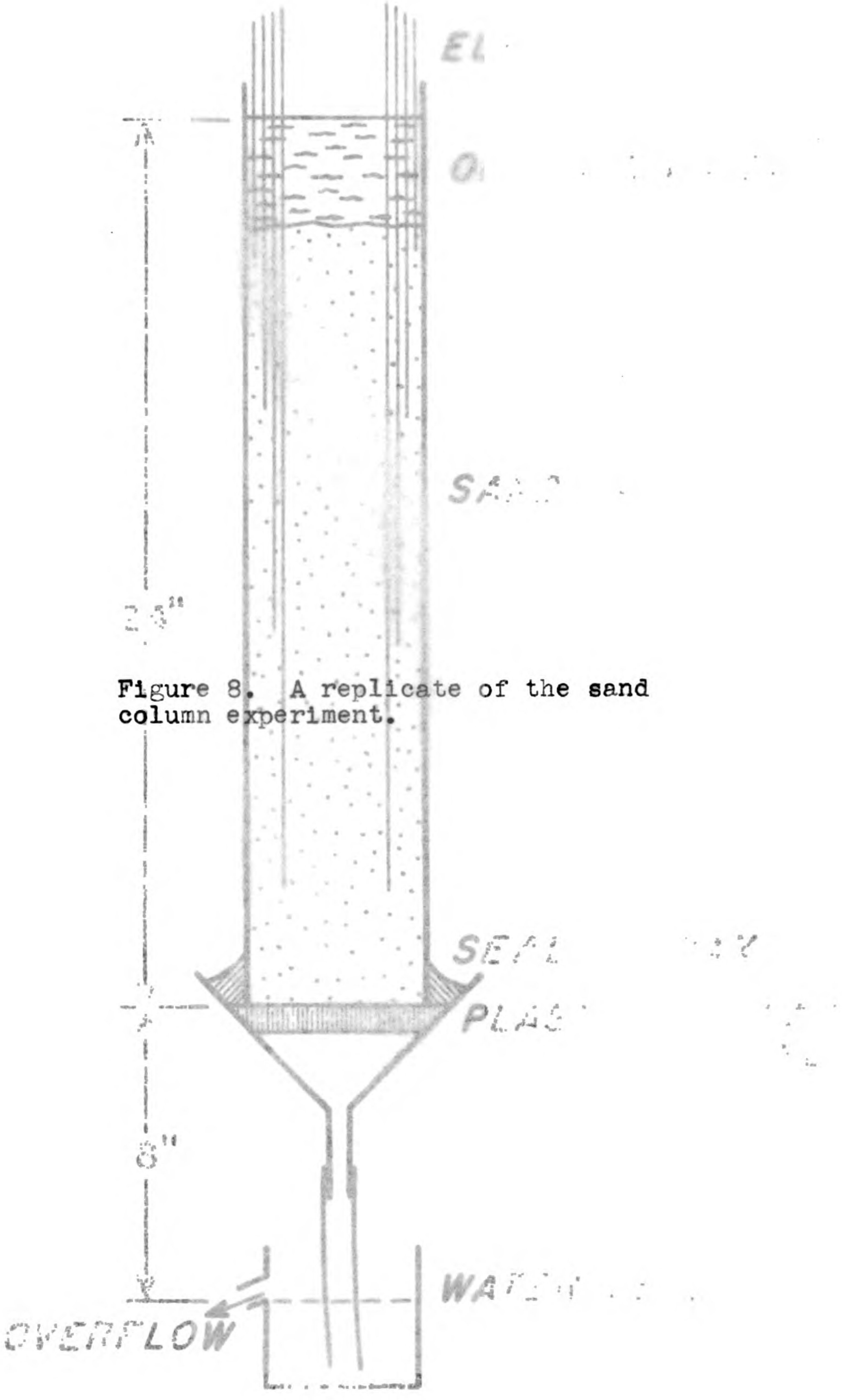
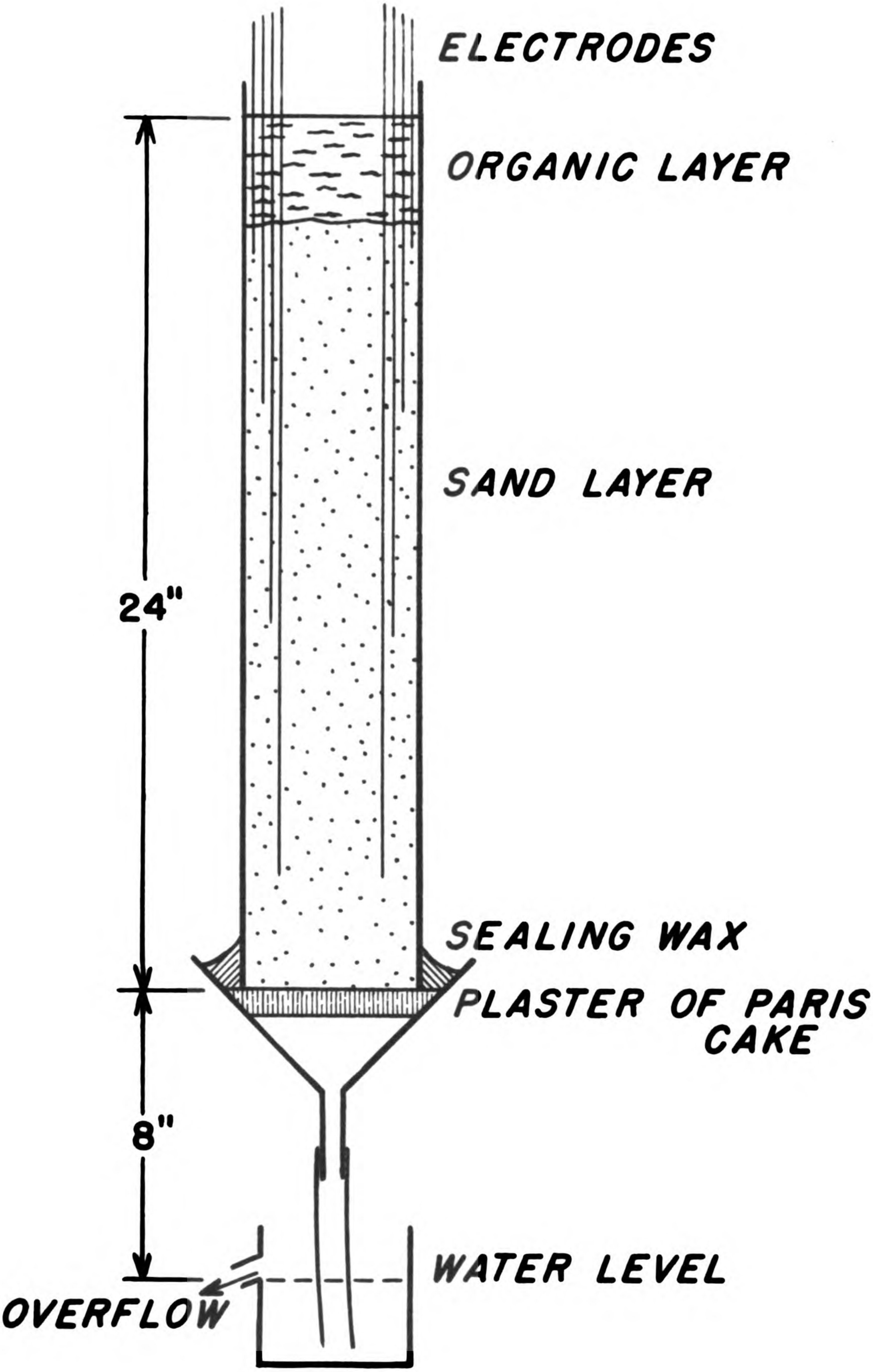


Figure 8. A replicate of the sand column experiment.


ELECTRODES
ORGANIC LAYER
SAND LAYER
24"
SEALING WAX
PLASTER OF PARIS CAKE
8"
WATER LEVEL
OVERFLOW

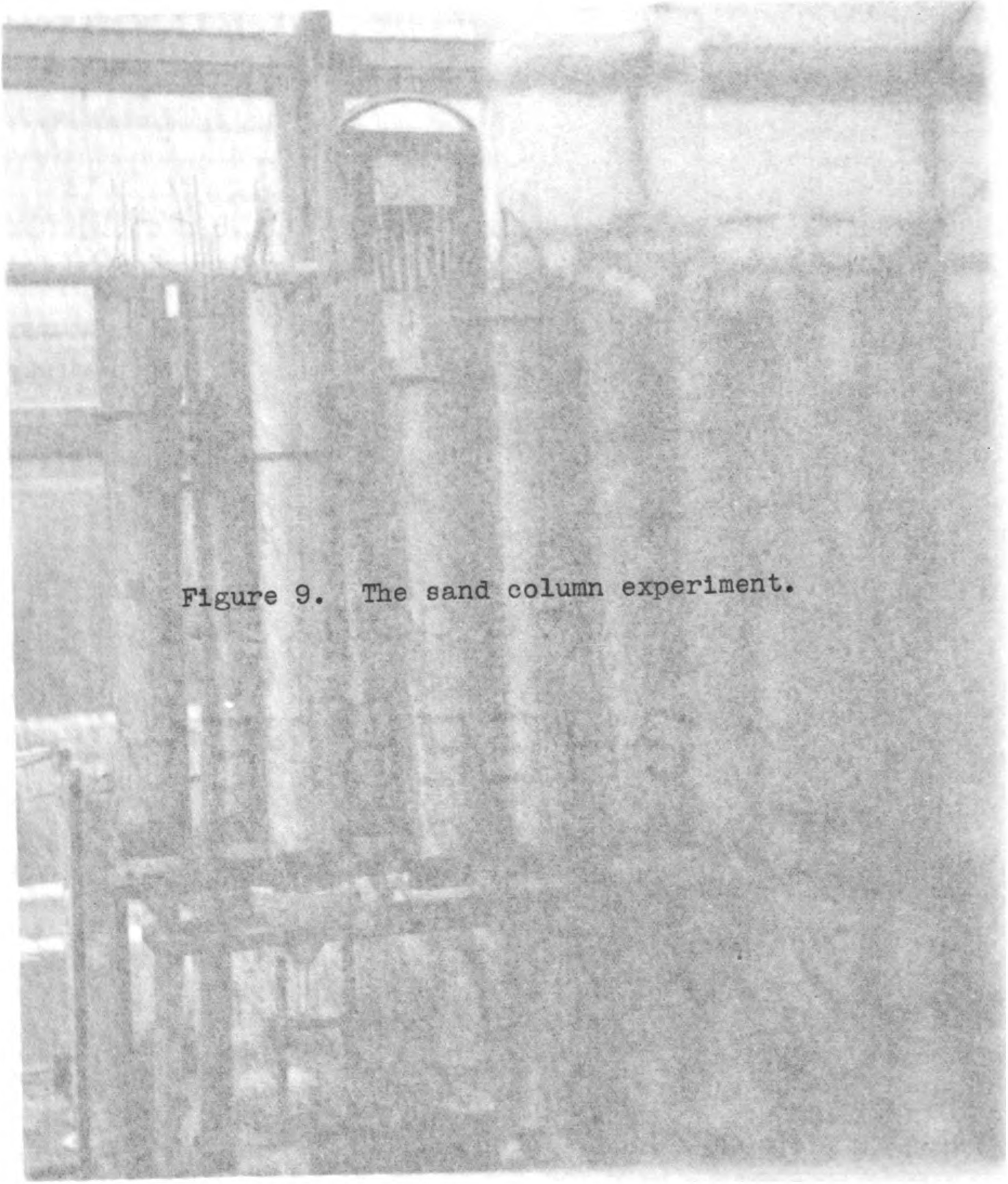
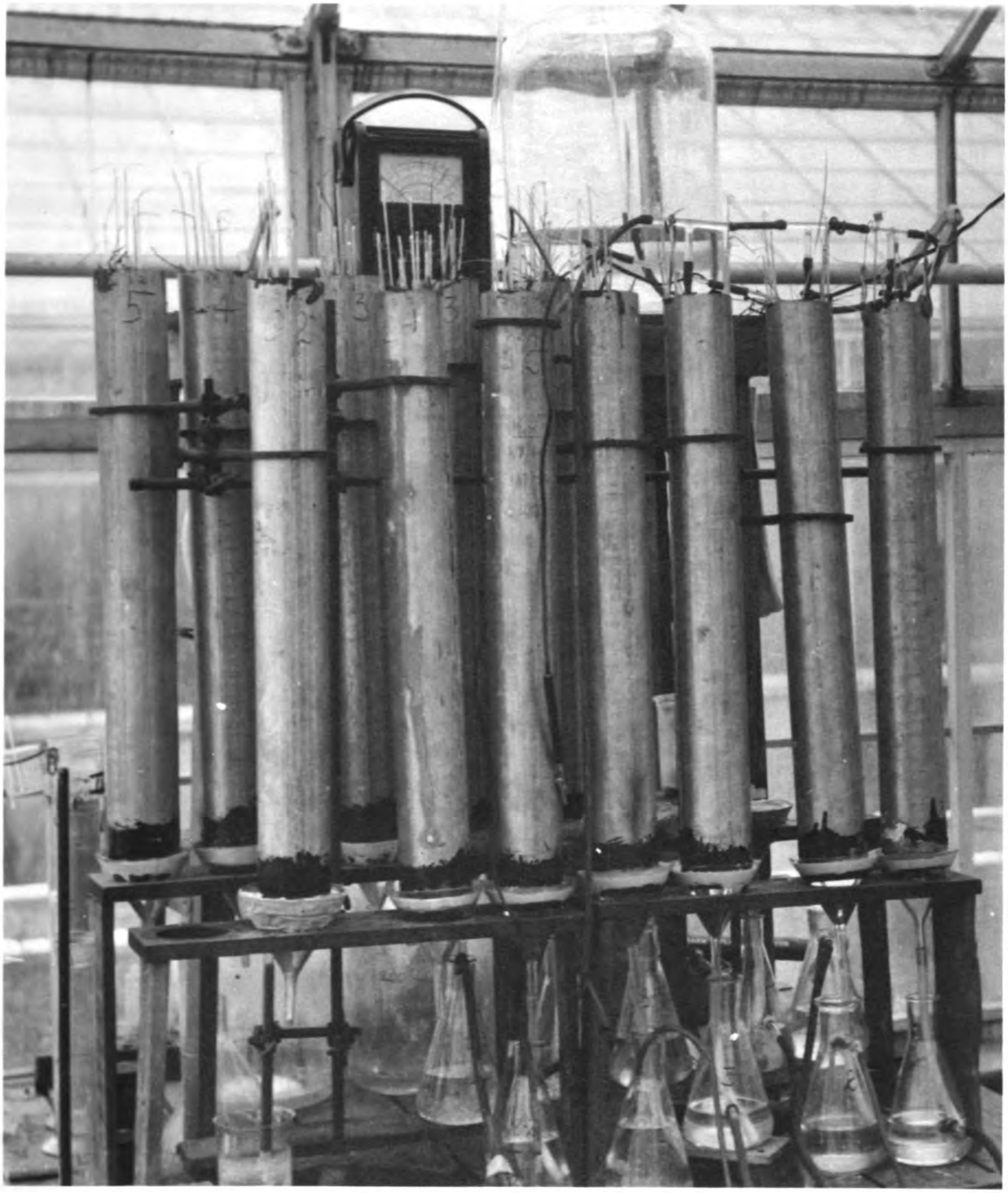


Figure 9. The sand column experiment.



Treatment A was continuous leaching with distilled water. Treatment B was leaching every three to four days, each time with 100 cc. of distilled water. Due to the continuous water flow, in treatment A, and the solubility of the Plaster of Paris used, it was very difficult to maintain the tension on the tables. In spite of these difficulties some results were obtained. The tension tables in treatment B worked very well throughout the course of the experiment. Redox potentials were measured every three to four days for six weeks using the Beckman vacuum tube potentiometer and the saturated calomel electrode in the same manner as for the field experiment. Results are shown in Tables II and III of the appendix and Figures 10 and 11 of the text.

At the same time, using the shiny platinum electrodes, and a specially prepared saturated calomel electrode, oxygen diffusion readings were obtained by the method of Lemon (18). The instantaneous readings are the initial swing of the ammeter needle and are a measure of the oxygen concentration at the electrode. The diffusion readings are a measure of the rate at which oxygen diffuses to the electrode. The results obtained are shown in Table IV of the appendix.

At the conclusion of the experiment, the sand columns were opened and examined. Samples of the sand taken at selected depths, were extracted with normal ammonium acetate solution buffered at pH 4.8 with acetic acid. The extracts were tested for ferrous iron using a modification of Olson's method (23) which uses o-phenanthroline as the color reagent. The intensity of color development was measured on the Coleman Junior Spectrophotometer set at a wavelength of 480 millimicrons. The extracts were then treated with hydroxyl amine hydrochloride to reduce all the iron to the ferrous form, and the iron was again determined. This gave a measure of the proportion of the total extractable iron that was ferrous in form. The moisture content of the samples was also determined at the same time. Results of the iron determinations are shown in Table I of the text and the moisture content of the sand columns at the time of opening in Table IV of the appendix.

RESULTS AND DISCUSSION

There is considerable variability between readings of electrodes in any horizon *in situ* due to the small portion of the soil body sampled. Variations in texture, structure, organic matter distribution, aeration, or moisture content of the soil as well as the proximity of the electrode to roots or worm channels cause variations in the redox potentials. Replacement of the electrodes during the course of the experiment indicated that the error was not due to effects on the electrodes themselves. The error caused by this variability could be evaluated statistically by the use of many replicates. Further error may be introduced unless care is used in the measurement of the potential in the field. Large junction potentials can be introduced unless care is used in making the contact between the calomel electrode and the soil.

In spite of the limited number of electrodes used in this exploratory field experiment the trends are very interesting. The results of the field experiment are shown in Figures 4, 5 and 6. The redox potentials for McBride fine sandy loam, Marlette loam and Parkhill loam are shown plotted against dates. The initial readings were taken immediately after the electrodes were inserted on April 28 and probably before they

Figure 10. Effect of depth on the redox potentials for treatment A of the sand column experiment.

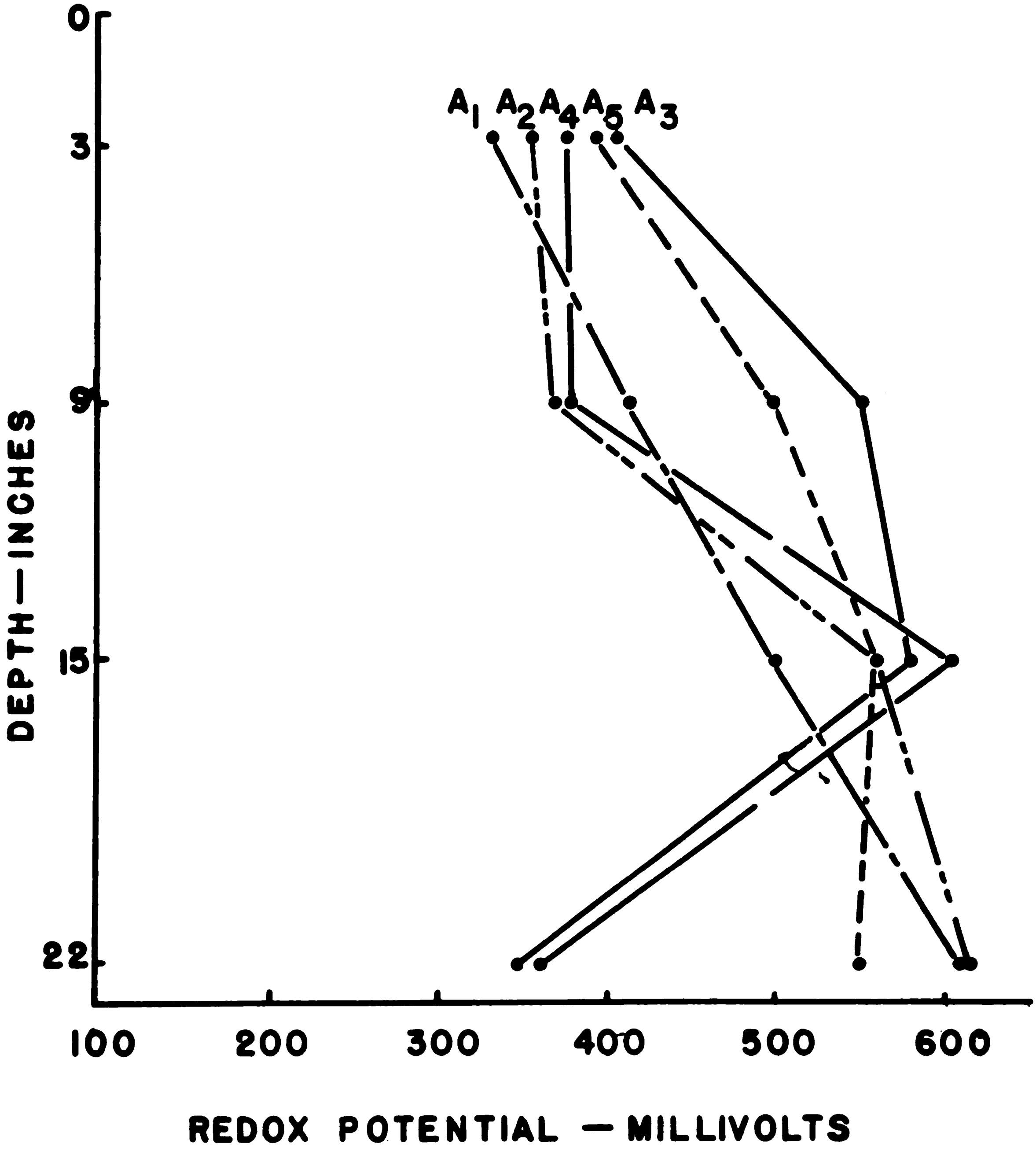
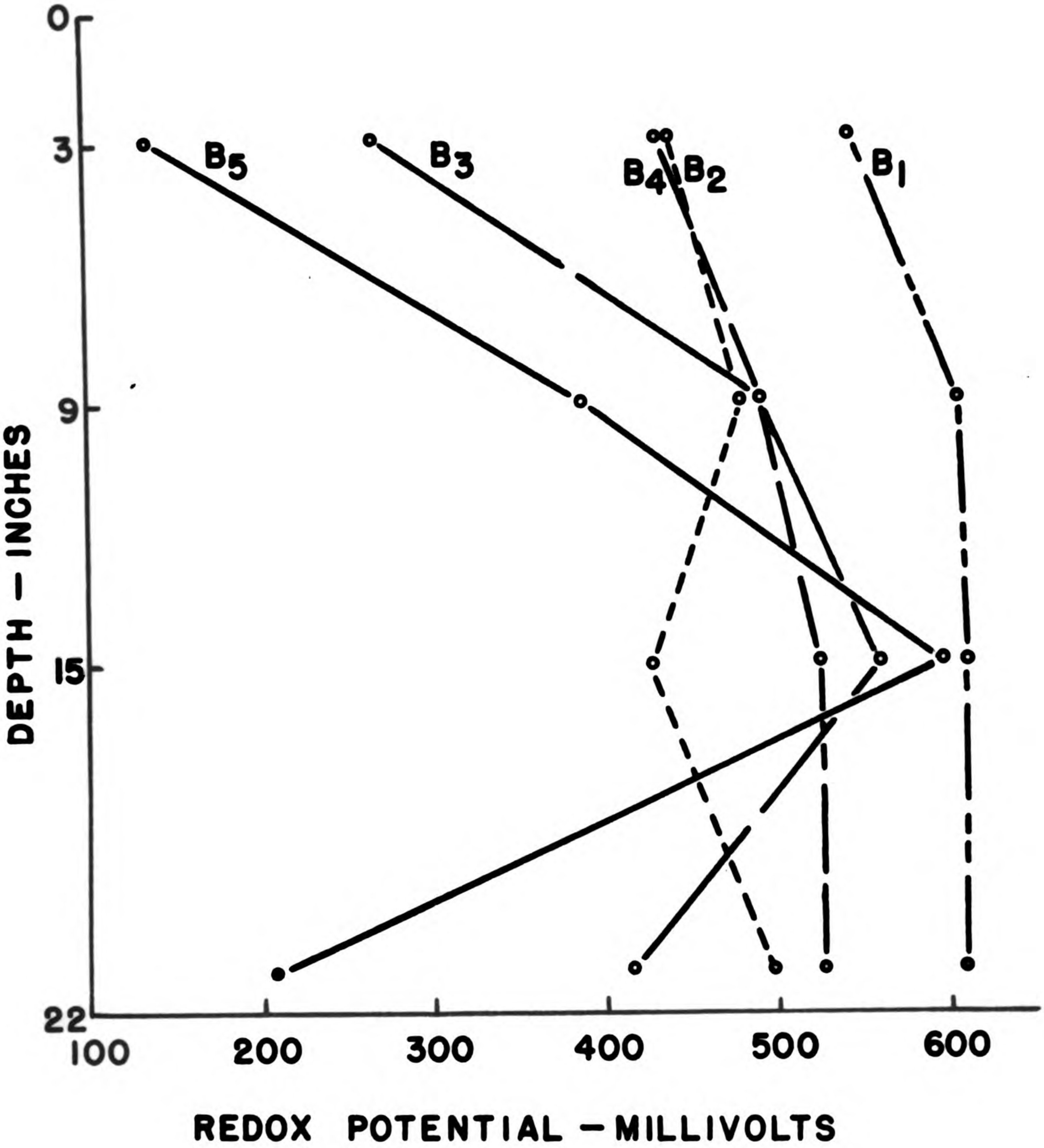

A1
A2
A4
A5
A3
0
3
9
15
22
DEPTH — INCHES
100
200
300
400
500
600
REDOX POTENTIAL — MILLIVOLTS

Figure 11. Effect of depth on the redox potential for treatment B of the sand column experiment.


0
3
9
15
22
DEPTH — INCHES
B5
B3
B4
B2
B1
100
200
300
400
500
600
REDOX POTENTIAL — MILLIVOLTS

came to equilibrium with the soil. After a week the soil had settled sufficiently that equilibrium was established. The redox potentials for McBride fine sandy loam Figure 4, had risen very high by the second week in May with little variations between horizons. In the Marlette loam, Figure 5, the redox potentials had not reached a level comparable to those in McBride fine sandy loam until the third week in May. They were also more variable between horizons than were those for the McBride in the first weeks.

Since both soils were well drained, the differences in redox potential were mainly associated with differences in texture throughout the profiles. McBride fine sandy loam dried out and warmed more quickly than did the Marlette loam. During the summer, the redox potentials for both soils were high, probably because of improved aeration. There was also a tendency for higher readings in the lower horizons than in the surface horizons.

It has been generally observed (6, 8, 11, 15, 16, 29, 34, 35) that organic matter tends to lower the redox potential of the soil. Since the surface layers of the soil, in general, contain more organic matter than the subsoil layers, these observations are substantiated in McBride fine sandy loam and Marlette loam. Figure 6 shows the results obtained in the poorly drained Parkhill loam. These results are of interest since this soil was waterlogged throughout the spring and the soil had not completely recovered from the effects of this condition until July 1st. The early readings were extremely low.

The readings were lowest in the twelve inch depth, indicating the zone of highest reduction in the profile. After July 1st, the redox potentials compared favorably with those of the well drained soils. These results indicate outstanding seasonal differences in the Parkhill loam as compared to the well drained soils; the difference being associated with variations in drainage.

In the sand column experiment, the redox potentials were treated statistically and checked by Nair's quick test (21). Treatment A was not considered a good test since the tension tables gave so much difficulty. However the means for both treatments are shown in Tables II and III in the appendix together with the statistical analysis for treatment B. Results for both treatments are similar. There is little difference between the general means for both treatments. The average redox potentials plotted against depths for five replicates are shown in Figures 10 and 11 for both treatments A and B. The potentials in the three inch depth were significantly lower (at the five percent level) than they were at lower depths. Oxygen diffusion readings by Lemon's method (18), shown in Table IV in the appendix, were also higher in the deeper portions of the profile. Examination of Table I shows that by far the greatest amount of ferrous iron was contained in the three inch layer. Generally the proportion decreased with depth in the column. This would indicate that iron was being reduced in the three inch layer. In this state iron is more soluble than in the ferric state. It could therefore move downward in the leaching waters to the lower levels. Since there existed in the soil column a state of higher oxidation in the lower levels, the ferrous iron could be oxidized to ferric iron and partially precipitated. Although certainly not conclusive, these data are considered as evidence of a possible method whereby iron may be translocated in the soil and precipitated in the B horizon.

TABLE I. FERROUS IRON CONTENT OF THE EXTRACTABLE IRON FOR TREATMENTS A AND B.

Depth Inches	Treatment A2	A3	A4	B1	B2	B5
3	52.5	55.0	47.5	38.5	42.5	52.0
9	14.1	40.0	37.5	18.4	16.8	14.2
15	13.0	13.2	26.5	15.3	24.3	28.0
22	10.6	15.2	18.0	12.6	32.0	30.5

This is not due to the redox potential itself, but to the combination of factors which results in the differential redox potentials.

If the process involved in the development of Podzols is defined as the translocation of sesqui-oxides from the A horizons and their precipitation in the B horizon, then the sand column experiment would indicate a possible mechanism important, among others, in the development of Podzols. The field results indicate that the season of the year when this process would be most active on well drained soils is in the early spring. More field studies are now underway.

The sand column experiment has shown that the use of sufficient replicates and a statistical treatment of the data is feasible when some of the variables are controlled. It may also be feasible to use statistical methods in the field and thus make it possible to overcome the large experimental error involved in the use of this tool.

SUMMARY

Redox potentials have been measured with variations in time and space in McBride fine sandy loam, Marlette loam, and Parkhill loam. In addition, redox potentials were studied in sand columns in a greenhouse experiment. The following observations were made:

(1) Extremely low redox potentials persisted until July 1 in poorly drained Parkhill loam.

(2) The potentials observed in the well drained McBride fine sandy loam, and Marlette loam, were high in early spring, indicating that the state of oxidation of these two soils would not limit plant growth, even early in the growing season.

(3) The Marlette loam showed a tendency toward a lower state of oxidation than McBride fine sandy loam until about May 12th.

(4) The protracted measurements of redox potentials of the various soil horizons in the field gives a more complete picture of the true organic conditions in the soil body.

(5) Redox potentials measured <u>in situ</u> may be useful as a tool for checking soil conditions affecting plant growth, particularly in the case of poorly drained soils.

(6) A redox profile has been observed in a laboratory study on sand columns which is submitted as evidence of a possible mechanism of Podzol formation. Reduced iron in solution was produced in the upper part of a well drained sand column. This could be precipitated lower in the sand column by oxidation. Redox potentials were significantly higher, oxygen concentrations were greater, and the proportion of soluble iron in the ferrous state was less lower in the sand columns.

(7) The sand column experiment indicates that many replicates and the use of statistical methods might make the use of redox potentials feasible in the field.

(8). It is suggested that the measurement of redox potentials may be useful in studies of soil formation, particularly of Podzols, Ground Water Podzols, and Humic Gley soils.

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APPENDIX

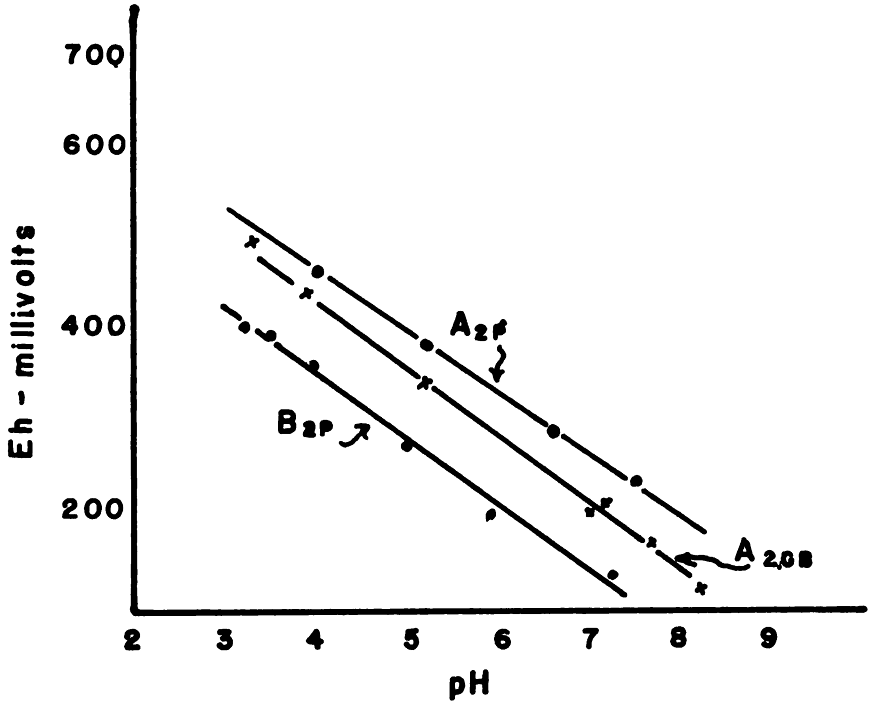

FIGURE 1. Eh - pH Relationship for McBride fine sandy loam.

TABLE I. AVERAGE VALUES OF FIVE REPLICATES OF TREATMENT A BY DEPTH AND DATES

depths dates	1	2	3	4	5	6	7	8	9	General Mean
3	420	409	388	367	369	412	221	491	322	378
9	439	430	435	463	490	488	365	444	392	438
15	554	553	539	608	601	572	520	544	575	563
22	482	498	495	583	575	508	485	489	357	497
Means	474	473	464	505	509	495	398	492	412	469
										469

TABLE II. TABLE OF MEANS FOR TREATMENT B OF THE SAND COLUMN EXPERIMENT.

depths dates	1	2	3	4	5	6	7	8	9	10	Means
3 in.	354	381	374	420	474	342	336	311	312	306	361
9 in.	477	499	477	513	549	477	479	470	487	475	490
15 in.	536	551	541	576	577	541	537	501	492	511	536
22 in.	416	420	446	448	460	478	488	456	457	453	452
	446	463	460	489	515	460	460	435	437	436	460*

*By using K.R. Nair's test (21) we find that the average for the three inch depth is significantly different from the general average and of course is significantly different from all the other averages.

TABLE III. ANALYSIS OF VARIANCE FOR DAYS, DEPTHS AND REPLICATES FOR TREATMENT B OF THE SAND COLUMN EXPERIMENT

	D.F.	S.S.	M.Sq.	F.	Nec.F.
Total	199	3,850,589			
Rep. (R)	4	1,393,499			
Depth (D)	3	829,499	276,500	3.08	2.67
Days (d)	9	117,170	13,019		
d • D	27	97,415	3,608		
D • R	12	1,076,077	89,673*		
d • R	36	109,512	3,042		
R•d•D	108	227,417	2,106		
Err.	156	1,413,006	8,564		

*Using the largest possible error term a difference of 83 millivolts or greater is significant at the five percent level.

TABLE IV. INSTANTANEOUS AND DIFFUSION READINGS FOR OXYGEN COMPARED WITH Eh READINGS FOR DEPTH IN TREATMENTS A AND B.

Electrode Set		Treatment A			Treatment B		
No.	Depth Inches	Eh. (MV)	Sim. O_2 (m.amps)	Dif. O_2 (m.amps)	Eh (MV)	Sim. O_2 (m.amps)	Dif. O_2 (m.amps)
1	3	221	4.64	2.94	309	4.68	2.34
2	9	365	3.76	1.74	473	12.9	9.23
3	15	520	6.18	3.30	506	17.62	12.64
4	22	485	6.42	2.72	455	16.72	7.59

TABLE V. MOISTURE VARIATION IN THE SAND COLUMNS WITH DEPTH FOR TREATMENTS A AND B.

Electrode Set		Moisture Content in Percent					
No.	Depth inches	A_2	A_3	A_4	B_1	B_2	B_5
1	3	8.	7.	9.	8.	7.	12.
2	9	12.	10.	11.	12.	9.	10.
3	15	14.	15.	13.	16.	14.	10.
4	22	16.	15.	17.	13.	13.	14.