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DIFFUSION, SORPTION AND DEPTH DISTRIBUTION
OF OXYGEN IN SOILS

by

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A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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INTRODUCTION

It is generally accepted that the composition and space of the soil atmosphere influence plant growth. Crop responses resulting from different management practices have usually been attributed to the composition and space of the soil atmosphere. Differences in bulk density, pore size distribution, aggregate stability, and other physical properties are also often interpreted in terms of aeration effects on soil. Because it is believed that excessive moisture contents in the soil result in poor aeration, large areas of agricultural lands are drained. The lack of response to improved fertility in a particular soil is usually attributed to poor physical conditions of the soil and more specifically to poor aeration of the soil. In spite of the generally accepted importance of aeration, there are few quantitative data on the subject.

Considerable research has been conducted in liquid and sand cultures on the effect of aeration of the root medium on the plant processes. The growth and development of roots, the growth and development of aerial portions of the plant, ion absorption, and water absorption are some of the major processes that have been investigated. Several good reviews of the literature have been made of these data and they will not be repeated here. In general, the research has demonstrated that the aeration status of the root medium influences

considerably the growth and development of roots. Not only is the growth and development of roots retarded by poor aeration, but the number of branches and root hairs are greatly reduced by poor aeration. It has been shown that the absorption and accumulation of ions by plants is directly related to the respiration of the plant roots. The absorption of water is also affected by poor aeration of plant roots. The exact role which poor aeration plays is not known but at least normal absorption of water by plants does not take place in a poorly aerated root medium. Most of the authors attribute the poor aeration to the lack of oxygen while some attribute it to the accumulation of carbon dioxide given off during respiration. A combination of the two conditions is probably the cause.

The major process by which oxygen is supplied and carbon dioxide is removed from plant roots is generally agreed to be diffusion. There has been extensive research in recent years on the effect of the physical properties of the soil on gaseous diffusion. The research has shown that increasing the bulk density, or increasing the moisture content, or in any other way decreasing the volume of air-filled pores in the soil, decreases the total quantity of gas diffusing through the soil. As these physical properties vary, so should the aeration status. Conversely, the aeration status should be a reflection of the physical properties.

The composition of the soil atmosphere is a result primarily of two processes, that of biological consumption and that of physical diffusion. But there is a lack of quantitative relationships between the composition of the soil atmosphere and the physical condition of the soil influencing diffusion.

In the diffusion process it has been suggested that gas movement through the thin film of water surrounding plant roots limits the amount of oxygen which can be supplied to the roots. The film of water may also limit the amount of carbon dioxide which can be removed from the plant roots. Because of the experimental difficulty in studying the liquid phase in soils, essentially no research has been done on the movement of gases through the moisture film.

The approach of identifying an aeration problem through a physical measurement or a group of measurements on the medium in which the plants are growing is at best rather indirect. A more positive approach would be to measure some biological process of the plant which is influenced by the aeration status of the medium. No one has developed a method of measuring a plant process which is influenced only by the aeration status of the root medium. The development of such a method lies in the realm of plant physiology and until such a method is developed quantitative measurements on the medium in which the roots grow offer the best solution to the aeration problem.

REVIEW OF LITERATURE

Composition of Soil Gases

The composition of the soil atmosphere was first given careful study in 1915 by Russell and Appleyard (50). They measured the oxygen concentration of the soil atmosphere at depths of 6 and 18 inches. Plots identified as located at Greatfield contained an oxygen concentration of 18.44% by volume at the 6-inch depth and 17.87% at the 18-inch depth. The plots located at Broadbalk contained an oxygen concentration of 20.52% and 20.33% at the 6-inch and 18-inch depths, respectively. The sampling procedure consisted of collecting the gas samples under a partial vacuum and analyzing the gas sample for oxygen content with a Haldane gas apparatus.

Following the work of Russell and Appleyard, little attention was given to the composition of soil gases until 1938 when Boynton and his co-workers (5, 6, 7, 8) began the collecting of considerable data on the composition of soil gases. The gas samples were also collected under a partial vacuum and analyzed with a Haldane apparatus. The authors were interested in the composition of soil gases in apple orchards on three soils: a sandy loam, a light silty clay loam, and a silty clay loam. Gas samples were taken throughout a five-year period at 1 foot increments to a depth of 6

feet. These data (8) are the first on aeration at considerable depths. On the sandy loam soil, the oxygen concentration at all depths remained high throughout the year. None of the samples were below 17% oxygen at any time during 1938. On the light silty clay loam and silty clay loam soils, however, the results were quite different. On the former, the oxygen concentration at all times of the year decreased with increasing depth in the soil profile. The first foot reached as low as 10% in April while the second foot reached as low as 4% during this same period. The oxygen concentration at the third, fourth, and fifth foot levels remained essentially zero much of the year. By the fall of the year, the oxygen concentration had increased at all depths so that there was a range of between 14% and 19% oxygen. The same trend in oxygen concentration was apparent on the silty clay loam soil but the condition was more exaggerated. Although the oxygen concentration in the first foot remained high throughout most of 1938, the second, third, fourth, fifth and sixth foot zones remained essentially zero throughout most of the year. The oxygen concentration at all depths increased in the fall of the year. A linear decrease of oxygen concentration with increasing depth was also apparent on the silty clay loam soil.

A summary of all the five years oxygen data, 1938 to 1944, on the apple orchards has been reported by Boynton and

Compton (6). In general, they found that the oxygen concentration in the sandy loam soil remained at a concentration almost that of atmospheric air during most of the growing season but, as the soil texture became heavier, the oxygen concentration decreased. On the silty clay loam soil, the oxygen concentration at the third foot level became as low as 4% in the early spring and, at the fifth foot zone, became as low as 2% during this same period.

Furr and Aldrich (21) measured the changes in oxygen concentration in irrigated date gardens on calcareous very fine sandy loam soil. The measurements were made at 6, 30, and 96 inch depths. The gas samples were also collected under a partial vacuum and analyzed with a Haldane apparatus. On infrequently irrigated plots, the oxygen concentration at the 6 inch depth fluctuated between 6% and 20% while at the 30 and 96 inch depths the oxygen concentration varied between 14% and 18%. The oxygen concentration on the frequently irrigated plots at the 6 inch and 30 inch depths became as low as 3% and remained that low for as long as 30 days. In the same period, the oxygen concentration at the 96 inch depth only became as low as 12%. These data suggest not only that the oxygen concentration is dependent upon the moisture content of the soil but that the oxygen concentration does not necessarily decrease with increasing depth in the soil profile.

The early work with oxygen composition of the soil atmosphere involved the collection of samples under a partial vacuum and analysis with a volumetric type of apparatus. The collection of gas samples under a partial vacuum, especially at shallow depths, may result in the contamination of the sample by mass flow of the free atmospheric air. Creation of a partial vacuum at some point in the soil tends to cause mass flow of air to this point. Air moves most rapidly by mass flow through the larger pores; therefore, a large pore extending from the point of sampling to the free atmosphere could cause considerable error in the gas composition of the sample. In any event, the sampling of a gas under a partial vacuum does not define the sampling region very adequately. The volumetric type of analysis used in the early aeration research was very laborious and time consuming. The amount of labor and time required are largely responsible for the lack of available data on oxygen composition of soil gases.

In 1945, Pauling et al. (43) developed a portable instrument for measuring the percent of oxygen in a gas sample. This development offered a convenient means of collecting data on the oxygen composition of soil gases.

Since the introduction of the Pauling oxygen analyzer, there have been a limited number of oxygen concentration measurements reported on field plots. One such experiment was made by Blake and Page (4) who measured the oxygen con-

centration on field plots in 1948 with the Pauling oxygen analyzer and reported only that during June and July the oxygen concentration did not fall below 18.5% at the 1-foot depth nor below 17.5% at the 3-foot depth

Likewise, Taylor and Abrahams (54) developed a method of obtaining gas composition data on soils without the possible error of collection of the gas samples under a partial vacuum. This method involved the measurement of the oxygen concentration in a chamber which was allowed to come to equilibrium by diffusion with the soil gas. These scientists measured the oxygen concentration in soil gases under corn and sugar beets to a depth of 12 inches. Their results show a linear decrease in oxygen concentration with increasing depth in the profile to the 12-inch depth measured. Oxygen concentration values as low as 10% were found at the 12-inch depth.

In these aerating studies, roots were growing in the soil. There appear to be no data on fallow soils although an interesting field of research would be to compare fallow and root conditions. This study is beyond the scope of the present thesis.

Diffusion of Gases through Soils

Diffusion is generally considered the principal means by

which oxygen is supplied to plant roots and carbon dioxide removed from the roots (12, 44).

One of the first men to study this diffusion of gases through soils was Buckingham (12) who measured the rate of diffusion of carbon dioxide and air through 8-inch cores of soil. The samples were of dry sand and dry soil as well as moist soil. The total pressure was maintained constant on both sides of the cores. By passing carbon dioxide and air over opposite ends of the cores, by measuring their rate of flow, and by measuring the content of carbon dioxide in the core both before and after passage of carbon dioxide over the surface of the soil, he determined the diffusion coefficient for carbon dioxide in the core. To calculate the diffusion coefficient, the data was expressed in an empirical equation. He found that the rate of diffusion of carbon dioxide and air was related to the porosity of the porous material by an equation $D = kS^n$ where D is the diffusion constant, S is the porosity, and k and n are constants. The constant n was found to be 2 on the materials he examined. The rate of the diffusion was thus a function of the square of the porosity. He concluded that the rate of diffusion of carbon dioxide and air did not greatly depend upon texture, structure, or moisture content of the soil but only on the square of the porosity.

Smith and Brown (52) repeated some of the work of

Buckingham but with more accurate methods of measurement. They maintained a closed volume which contained carbon dioxide at one end of an undisturbed soil core and passed air over the other end of the core. The total pressure was constant on both ends of the core. The carbon dioxide concentration in the closed volume was measured with time, and the diffusion constant was determined by an empirical equation.

$$D = XH / [760 At (C_1 - C_2)] ,$$

where D = the diffusion constant

X = the volume of carbon dioxide passing through the core of soil (0° C. and 760 mm.)

H = the height of the column of soil in cm.

C₁ = the concentration of carbon dioxide on the lower face of the column of soil

C₂ = the logarithmic average of initial and final concentration of carbon dioxide on the upper face of the column of soil

A = the cross sectional area

t = the time in seconds.

The authors found that the diffusion of carbon dioxide through cores of moist soil was complicated by the production of carbon dioxide to such an extent that an accurate determination could not be made. Brown and Smith suggested the same possible error in the Buckingham data. Using air-dry soil, the scientists were able to determine the rate of diffusion

of carbon dioxide through soil in relation to porosity.

The relationship of the rate of diffusion to porosity was found to be $D \times 10^7 = 2.297S + 1.402$, where D is the diffusion constant and S is the porosity.

Penman (44) not only developed the theory for steady and nonsteady state of diffusion through porous media but also applied these theories to the diffusion of carbon disulfide and acetone through several porous media. For the steady state of diffusion of a gas through a porous solid:

$$dq/dt = - (D/B) A (P_2 - P_1)/L , \quad (1)$$

where D = the diffusion coefficient

A = the total cross-sectional area

L = the length of the volume of solid

$P_2 - P_1$ = the partial pressure at the ends of the volume of soil

B = a proportionality constant

q = the quantity of gas diffusing in time t .

When the effective cross-sectional area is SA and the effective length of path is L_e , the equation (1) becomes

$$dq/dt = - (D_0/B) S A (P_2 - P_1)/L_e ,$$

where S = the porosity

D_0 = the diffusion coefficient in air,

or the relationship between the rate of diffusion and porosity is

$$D/D_0 = (L/L_e) S.$$

Penman found that, for a number of porous solids and for a limited range of porosity (0.0 to 0.7), the equation $D/D_0 = 0.66S$ was a good approximation. This equation appears to hold regardless of the nature, texture, or structure of the material. Since he used in this study acetone and carbon disulfide (which is a soil fumigant), the production or consumption of a gas did not complicate the determination. In a later paper, Penman (45) studied the diffusion of carbon dioxide through porous medium other than soil and found that the relationship to porosity was the same as reported in the previous paper. He suggests the possibility that in field soils, because of microbial activity, the determination of the rate of diffusion may be very complex.

Hogan (27) measured the rate of diffusion of carbon disulfide through soil and used an empirical equation to report his data. His equation was similar to the theoretical equation developed by Penman for steady state diffusion. Hogan found that the rate of diffusion of carbon disulfide was a function of the porosity. The relation between porosity and diffusion, for Yolo fine sand, had an intercept on the porosity axis at 26%. By comparison, the rate of diffusion through a fine sandy loam, loam, and clay had intercepts at porosities between 24% to 28%. Moreover, he found that the rate of diffusion through cores of soil decreases with

increasing bulk density.

Taylor (55) modified the equation of Penman and expressed the ratio of the rate of diffusion through a porous medium to the rate of diffusion through air as $D/D_0 = 1/n^2$ where $1/n^2$ is a parameter called the "equivalent diffusion distance". This "equivalent diffusion distance" is a soil parameter which Taylor suggested as a measure of soil aeration. Taylor also measured the diffusion of oxygen through powdered glass, sand, and soil. He found the relationships between $1/n^2$ and porosity to be $1/n^2 = 0.668S$ where S is the porosity. He made, however, no attempt to account for the oxygen that would be consumed in moist soil during the measurements of rate of diffusion through soil.

De Vries (15), who has given a discussion of the constant 0.66 in Penman's equation relating D/D_0 with porosity S , considers that the relationship of D/D_0 with the porosity of the porous medium depends upon the shape of the particles. Disk shaped particles and spherical particles give a non-linear equation for D/D_0 as a function of porosity but the largest deviations from linearity are encountered when disk shaped particles are used.

Van Bavel (57) was one of the first to take into consideration the consumption or liberation of a gas in the equation for the diffusion of gases through soil. Through a solution of the Poisson equation, Van Bavel developed the

equation for the partial pressure of a soil gas at any depth in the soil. This partial pressure of a gas at any depth depends not only on the specific diffusion impedance but also on the rate of consumption or liberation of the gas. One of the major contributions of this theoretical approach is that it demonstrates the relative unimportance of surface crust in the overall aeration of deep permeable soils. It is notable also that Van Bavel's work indicated a factor 0.6 between D/D_0 and the porosity rather than 0.66 found by Penman.

On the other hand, Blake and Page (4), who measured the rate of diffusion in field soils using carbon disulfide, were not concerned with the consumption or the liberation of a gas. For Paulding clay, these scientists found the relationship between D/D_0 and porosity to be linear with a constant equal to 0.618. In Brookings clay, Blake and Page found $D/D_0 = 0.7985$. The curve for Brookings clay did not approach the origin but intercepted the porosity axis at 10% porosity. This was undoubtedly due to blocked pores that contributed to the porosity but not to the diffusion. The authors suggested that the constant in the relationship between the rate of diffusion and porosity depends upon the porous material and may be different for each soil.

Raney (48) developed a field method for determining the rate of diffusion of oxygen in soil. He studied the

effect of tillage on the rate of diffusion in soil. In general, he found that tillage treatments which resulted in higher bulk density gave lower diffusion rates. Lower diffusion rates were also obtained in soils of high moisture content.

In the present study, an equation relating porosity and diffusion which intercepts the porosity axis was found. For diffusion in soil, equations of this type were also found by Blake and Page (4), Hogan (27), and Smith and Brown (53).

Solubility of Gases in Water

Theoretical considerations

The solubility of a gas in pure water depends upon the temperature and pressure of the system. The phase rule (32, p. 693) shows how the number of degrees of freedom F of the system is related to the number of components C and of phases P present at equilibrium. This rule states that $F = C - P + 2$. Since there are 2 components and 2 phases in a gas-water system, there are 2 degrees of freedom. Thus both temperature and pressure must be fixed in order to specify a definite quantity of gas dissolved in pure water.

The quantitative relationship between the solubility of a gas and the pressure of the gas at a temperature above its

critical temperature is referred to as Henry's law (42, p. 18). Henry's law is expressed mathematically by $P = kX$ where P is the equilibrium pressure, X is the mole fraction of the gas, and k is a proportionally constant. Most gases obey Henry's law if the temperatures are not too low or the pressures not too high and particularly if the gas is only slightly soluble. From this relationship, it is apparent that an increase in partial pressure results in an increase in the quantity of dissolved gas.

The quantitative relation between the solubility of a gas and temperature may be shown by considering the Clausius-Clapeyron equation (32, p. 695)

$$d \ln c/dT = \Delta H/RT^2$$

where c is the concentration of the gas in the liquid phase in moles per liter of water, ΔH is the differential heat of solution of one mole of gas in a saturated solution at temperature $T^\circ K$, and R is the universal gas constant. If ΔH is assumed to be independent of temperature, then integration of the above equation gives

$$\ln c_2/c_1 = -\Delta H/R (1/T_2 - 1/T_1) .$$

Since ΔH is almost always negative, it is apparent that an increase in the temperature of the system results in a decrease in the solubility of the gas.

If we are concerned with the solubility of a gas in water that also contains electrolytes, the system will have

3 degrees of freedom since there are 3 components. Thus, in addition to the temperature and pressure, the concentration of the electrolyte must be fixed in order to specify a quantity of dissolved gas. As a general rule, gases are less soluble in aqueous salt solutions than they are in pure water and this phenomena is commonly referred to as the "Salting-Out Effect".

Albright and Williams (3) have given an explanation for the effect of salts on the solubility of non-electrolytes. According to them, an electric charge, such as an ion, attracts the medium of highest dielectric constant. Since the dielectric constant of water is more frequently higher than that of other neutral materials, it usually happens that water is preferentially pulled into the field existing about the ion. In such cases the less polar non-electrolytes members are forced into the portion of the solution remote from the field of the ions. This results in an increase in the non-electrolyte to water ratio in the regions and a reduction in the solubility of the non-electrolyte when referred to the total water present.

Solubility of oxygen in pure water

The solubility of oxygen in pure water has long been a subject of experimentation. Slightly different values have

been reported for different methods of analysis. Analyses have been made using volumetric techniques whereby the volume of oxygen dissolved by a given quantity of water is determined. There have also been methods used whereby the amount of gases dissolved in a given quantity of water is determined chemically. Numerous values for the solubility of oxygen in water have been reported but only a representative number will be given in this review.

Fox (20) has determined the solubility of oxygen in pure water at different temperatures by a volumetric method and developed an equation to express his data from 0° to 50° C.

$$1000a = 49.234 - 1.344T + 0.028752T^2 - 0.0003024T^3,$$

where 1000a is the volume in cc. of oxygen at 0° C. and 760 mm. pressure dissolved by 1000 cc. of distilled water, and T is the temperature in degrees Centigrade. For 25° C. the volume of oxygen dissolved by 1000 cc. of distilled water becomes 28.879 cc. With a partial pressure of oxygen of 760 mm., this gives a value of 3.27×10^7 for Henry's constant.

Whipple and Whipple (58) used the Winkler chemical method to determine the dissolved oxygen in pure water and reported a value at 25° C. of 8.35 ppm. This was for air-saturated water which was exposed to 760 mm. in total pressure and an oxygen concentration of 20.9%. With a partial pressure of oxygen of 158.8 mm., this gives a Henry's law constant of 3.38×10^7 .

The International Critical tables (28) have recorded values for Henry's law constant which differ depending on volumetric or titration analysis. For volumetric analysis the value given at 25° C. is 3.33×10^7 . For the method of titrating oxygen in air-saturated water the value at 25° C. is 3.27×10^7 .

Truesdale et al. (56) have summarized the data of several research workers on the solubility of oxygen in air-saturated distilled water. At 25° C. they found values ranging from 8.16 to 8.46 ppm. of oxygen. They also found that over the temperature range of 0-36° C. the solubility of oxygen in air-saturated water followed the equation

$$C = 14.161 - 0.3943T + 0.007714T^2 - 0.0000646T^3 ,$$

where C is the solubility concentration in parts of oxygen per million parts of water, and T is the temperature. At 25° C. this gives a value of 8.12 ppm. Henry's law constant for 8.12 ppm. of oxygen and a partial pressure of oxygen of 158.8 mm. is 3.47×10^7 .

There appears to be no consistent value for the solubility of oxygen in pure water. The value 3.33×10^7 reported in the International Critical tables for Henry's law constant for oxygen solubility in pure water determined by a volumetric technique appears to be a good average value and will therefore be used in the calculations involved in this investigation.

Solubility of helium in pure water

Most of the experimental data on the solubility of helium in pure water is reported in terms of the Bunsen absorption coefficient. The Bunsen absorption coefficient is defined as the volume of a gas reduced to 0° C. and 760 mm. pressure dissolved by an equivalent volume of the absorbent when the partial pressure of the gas itself is 760 mm. Essentially all of the determinations on the solubility of helium were determined by measuring the volume of the gas dissolved by a given quantity of water. Cady et al. (13) have determined the solubility of helium in pure water at 25° C. and they have obtained values for duplicate determinations of 0.00859 and 0.00862. Lannung (32) determined the solubility of helium in pure water and he reports a Bunsen absorption coefficient of 0.0087 at 25° C. Wiebe and Gaddy (59) determined the solubility of helium in pure water at 25° C. and obtained an absorption coefficient of 0.00860. They found that the absorption coefficient as a function of temperature reached a minimum at about 30° C. They also compared their determinations with other workers. Akerlöf (2) determined the solubility of helium in pure water at 25° C. and obtained a value of 0.00860. With the exception of the data of Lannung, the absorption coefficients of all other workers are in good agreement. The value of 0.00860 seems to be the most correct

value for the solubility of helium in pure water at 25° C.

Solubility of oxygen in water
containing electrolytes

It has been known for some time that the presence of electrolytes in water decreases the solubility of oxygen in that water. As stated before this effect has been referred to as the "Salting-Out-Effect". Much of the early work on this effect has been reviewed by Randall and Farley (47). Since then others have presented simplified equations for which the solubility of oxygen in water containing varying amounts of salts could be calculated (56, 58). The extent of this effect is evident from the following data which was taken from the International Critical tables (28, p. 271). It should be noted that the Bunsen absorption coefficient for pure water at 25° C. is 0.02822.

<u>Electrolyte</u>	<u>Normality</u>	<u>Absorption coefficient of oxygen at 25° C.</u>
HCl	0.5	0.0271
	1.0	0.0263
	2.0	0.0245
NaCl	0.5	0.0240
	1.0	0.0204
	2.0	0.0145
NaOH	0.5	0.0229
	1.0	0.0187
	2.0	0.0122
KOH	0.5	0.0231
	1.0	0.0189

From the above data, it is apparent that the presence of the electrolytes in water decreases the solubility of oxygen from that in pure water. It is also apparent that the solubility of oxygen decreases as the concentration of salt increases.

It is to be expected that the presence of colloidal material and particularly colloidal electrolytes should also influence the solubility of oxygen in water. While there is no evidence in the literature on their effect on oxygen solubility, Findlay and Creighton (18, 19) have observed a variable but pronounced effect of such materials on the solubility of H_2 , CO_2 , and NO_2 . Simmons (51) on the other hand concluded that the presence of colloidal clay in water did not affect the solubility of CO_2 .

Gas Adsorption by Soils and Clay Minerals

The phenomena of physical adsorption of gases by solids has been reviewed by Brunauer (10). This subject has also been dealt with in considerable detail in several other text books (1, 35).

The subject of gas adsorption has received considerable attention in the field of soils because it can be made use of in the measurement of surface areas of clays and soils. In the process of these measurements it has become obvious that

the nature of the clay mineral, the exchangeable cations, and the presence of residual water have an extremely important effect. Thus in recent years much attention has been devoted to a study of these factors and indirectly to the use of gas sorption in the characterization of clay minerals.

The first application of the BET Theory to the measurement of surface area in soils and their colloidal fraction was made by Brunauer and Emmett (11). They determined the nitrogen adsorbed by Cecil soil, Cecil colloid, Barnes soil and Barnes colloid at the temperature of liquid nitrogen and calculated surface area of these materials to be 32.3, 58.6, 44.2, and 101.2 m²/gm., respectively.

In a later paper, Emmett, Brunauer, and Love (16) studied the adsorption of several gases on the same materials at -183° C. and at 0° C. Furthermore they started with air-dry samples and determined the effect of time and temperature of evacuation on the areas obtained. They found that the samples had to be evacuated for 20 to 90 hours before constant values were obtained. Apparently the residual water influenced the gas sorption. In contrast to the S-shaped isotherm obtained at -183° C. the adsorption of nitrogen and oxygen at 0° C. was a linear function of the pressure. There was a slightly greater adsorption of nitrogen than oxygen at any given pressure.

Makower et al. (33) applied the method of Brunauer to

determine the surface area of several soils. They also studied the adsorption of carbon dioxide, nitrogen, and oxygen at 0° C. The adsorption of nitrogen and oxygen at 0° C. was a linear function of the pressure. It may be estimated from their plotted data that about 0.1300 of oxygen was adsorbed per gram of Cecil soil at 0° C. and 1 atmosphere pressure. The adsorption of carbon dioxide as a function of pressure appeared to be linear up to about 20 cm. of Hg and then decreased in slope to 1 atmosphere. The order of magnitude of the quantity of carbon dioxide adsorbed at 0° C. was much greater than either oxygen or nitrogen.

Nelson and Hendricks (39) determined the specific surface of soils, soil colloids, and some clay minerals by applying BET Theory to nitrogen and ethane adsorption measurements at -195° C. and -78° C., respectively. In these experiments they had to evacuate their samples for about a day at room temperature before the adsorbed gases and water vapor was sufficiently removed. They studied the effect of heating pure clay minerals on the surface area of the clay minerals. They found that the surface area of Kaolinite changes very little when heated from 30° C. to 900° C. On the other hand, they found that the surface area of Illite decreased when the clay mineral was heated from 30° C. to 700° C.

Jamison (29) studied gas adsorption as it related to errors in the pycnometer method of determining porosity. He

found that as the soil became dryer the error in his porosity measurements increased because the gas was adsorbed by the soil particles. In their oven-dry state the Hurricane and the Lloyd soil adsorbed 15.3 and 3.7 cc. of air per 100 grams of soil, respectively, at 23° C. and 1 atmosphere pressure. This adsorption of gas disappeared when the water content of the soils was increased to 10% (100 atm. tension) in the case of his Hurricane soil and 20% (15 atm. tension) in his Lloyd soil. The amount adsorbed was a linear function of the pressure both for air-dry, and oven-dry soils.

Recently Escard (17) and Brooks (9) have made a careful study of the nitrogen adsorbed by the clay minerals and the effect of the exchangeable cations and residual water on this adsorption. In general Brooks concluded that nitrogen adsorption is strongly influenced by the water content in clays like montmorillonite and illite which are characterized by a large cation exchange capacity and small particles. Clays such as kaolinite and pyrophyllite which have large particle size and low cation exchange capacity show little effect of water content on nitrogen adsorbed. In the case of kaolinite, illite, pyrophyllite and sodium bentonite, the nitrogen is adsorbed only on the external surfaces and thus provides a measure of external surface area. Calcium bentonite on the other hand adsorbs some nitrogen between the plates when the clay is partially dried. From accompanying X-ray data, this

appears to be due to the fact that the contraction of the lattice lags behind the loss of water.

Gregg and Stephens (24) measured the surface area of kaolinite when it was heated up to 800° C. They found very little change in the surface area as kaolinite was heated to 800° C. In an earlier paper, Gregg (23) states that vermiculite increases in surface area as the mineral loses its water of hydration by heating but no experimental evidence is presented.

Lamb and Woodhouse (31) studied the effect of water content in the adsorption of carbon dioxide, oxygen, and hydrogen on chabasite. They found the maximum adsorption of the gases occurred when the material was 93% to 98% dehydrated. There was a linear increase in O_2 adsorption as chabasite was dehydrated up to 98%.

Considerable attention has also been given to the adsorption of NH_3 on clay materials (14, 38, 53). As suggested by Emmett et al. (16) the adsorption of NH_3 may, however, involve specific chemical adsorption effects not encountered in nitrogen adsorption. The very high heat of adsorption of NH_3 on bentonite indicating a strong bond between the ammonia and the clay surface observed by Mortland (38) appears to substantiate this suggestion.

The adsorption of water vapor by soils and clays has also received a great deal of attention (30, 36, 37, 40, 41,

42). The polar water molecules penetrate between the lattice layers of the expanding lattice minerals. Thus several attempts have been made to use water vapor adsorption isotherms in surface area measurements to include both external and internal surfaces. This use of water vapor sorption isotherms has very recently been reviewed and criticized by Quirk (46). The adsorption of water vapor accompanied by other techniques, particularly X-ray measurements, has also been used to elucidate the nature of water layer on the surface of silicate minerals and the effect of the exchangeable ions in this water layer. At the present time there is no general agreement as to the precise nature of this first layer of water but it appears likely that the water molecules do not form a close packed monomolecular layer. In fact the single crystal X-ray analysis of magnesium vermiculite by Matheson and Walker (34) indicates that the intercrystalline water is oriented around the magnesium ions in such a manner as to provide each cation with 12 fold coordination and at the same time form a hexagonal network layer on the silicate surface. The significance of this water layer on silicate surfaces to other gas sorption studies lies in the fact that the hexagonal holes in this water layer may provide access for gas sorption by the clay even though water is present.

METHOD OF APPROACH

What little research has been done on gas composition of the soil atmosphere under vegetation has been limited to survey type experiments for particular crops. Practically no research has been conducted on the composition of the soil atmosphere in relation to the physical properties of the soil. When research workers have found, through measurements, that such physical properties have been improved (lower bulk density, higher hydraulic conductivity, and greater water stability), these workers have inferred, but without measurements, that the diffusion rate has increased and that there is more oxygen and less carbon dioxide in the soil. In short, they affirm that the "aeration status" has been improved.

In 1952, however, synthetic organic materials were developed which offered a research tool for studying the improvement of soil structure in relation to the composition of the soil atmosphere, since they exhibited remarkable powers of stabilizing soil aggregates. These materials had the potentialities of improving soil structure in general farming operations as well as in improving structure in research studies. With these synthetic organic materials, the soil structure could be improved without introducing other factors such as fertility and microbial stimulation.

Two aeration experiments were, therefore, established with these synthetic organic soil conditioners, one on Edina silt loam soil, and the other on Webster silty clay loam. The Edina silt loam soil has a silt loam surface but, at about 18 inches, has a heavy clay "B" horizon which is generally believed to be poorly aerated and restrictive to plant root development. The Webster silty clay loam is very productive but frequently requires drainage. This soil is drained because drainage is believed to improve soil aeration. Having applied the synthetic organic conditioners to the surface 6 inches of these soils in order to improve the stability of the soil aggregates, the effect of the materials on the stability was measured by a wet sieve procedure. The oxygen composition of the soil atmosphere was then measured at approximately one month intervals throughout the growing season. In addition, the potassium content of corn leaves was also determined since potassium absorption has been shown to be affected by the aeration status of the plant root medium. The analyses were made on corn leaf samples taken when the corn was at the 75% silking stage. Other measurements were likewise taken to determine the effect of the synthetic soil conditioners not only on the moisture content of the soil both in the treated zone and in other horizons, but also on crop production as measured by corn yields.

Diffusion is believed to be the major process responsible

for the supply of oxygen to plant roots and for the removal of carbon dioxide from plant roots. The diffusion is expressed through a function of the percentage of air space in a soil, that is, the aeration porosity. Some research has indicated that diffusion rate is related to the square of the porosity but most research indicates a linear relationship. The constant relating porosity to the diffusion constant has been found to be 0.6 to 0.7 for porous media other than soil. The same figure has also applied to some soils.

Considerable emphasis is being placed at the present time on the measurement of the diffusion constant of a gas, particularly of oxygen, in soils. It is believed that these constants are a measure of the oxygen supplying power and the carbon dioxide removing power of the soil. Such diffusion constants should then be a measure of the ability of the soil to supply oxygen to plant roots and to remove carbon dioxide from plant roots. A soil with a large diffusion constant would be a better medium for plant growth, as far as aeration is concerned, than a soil of low diffusion constant.

It has been demonstrated that the liberation of carbon dioxide in moist soils influences the determination of the diffusion constant of carbon dioxide in soils. It seems likely that the consumption of oxygen by soil microorganisms influences the determination of the diffusion constant of

oxygen in soils. Studies have not been made where the diffusion of oxygen or carbon dioxide takes place during the controlled consumption or liberation of gases. Diffusion measurements during controlled consumption or liberation will give information not only on the effect of consumption or liberation on determining the diffusion constant itself but will also give information on the relative importance of consumption and liberation on the total quantity of gas supplied or liberated.

An experiment was designed where the diffusion of oxygen through laboratory prepared soil cores was studied when consumption and when no consumption of oxygen by microorganisms was involved. Phenol solutions were used to prevent consumption in soil cores, sucrose solutions to stimulate microbial consumption of oxygen. The diffusion of oxygen through the cores was studied and the effectiveness of the phenol in reducing consumption was tested.

An aspect of soil aeration which has received essentially no attention is the relation of the amount of soil oxygen to the amount of soil water. It has been known for a long time that oxygen is dissolved in pure water and aqueous solutions. It has also been observed that oxygen is adsorbed on solid particles of soil. The adsorption of oxygen and other gases by soil particles has been used for the determination of surface area of the soils and soil colloids. The question thus

arises: Does water which is adsorbed by the solid particles dissolve oxygen as readily as does free water and is oxygen which is adsorbed on dry solid particles removed by the water when the particles are settled? An answer to these questions is sought in this thesis.

It has been shown that several factors influence the amount of oxygen which the soil water will dissolve. It has been demonstrated that the presence of salts in water reduces the solubility of oxygen. But the soil solution is known to contain salts as well as ions associated with the solid particles. Thus, the salt concentration of the soil solutions, which becomes more concentrated as the soil becomes dryer, should affect the solubility of oxygen in soil solution. Since the soil particles have a charge and are known to adsorb water, the particles themselves may also affect the solubility of oxygen in the soil water.

Dry soil particles are known to adsorb oxygen. If the soil particles adsorb oxygen when they are moist, this should affect the sorption of oxygen by the soil-water system. The quantity of oxygen that soil adsorbs at different moisture contents thus becomes of practical importance.

Investigations were, therefore, conducted on the field and laboratory aspects of soil aeration; the oxygen concentration of the soil atmosphere was measured on synthetic aggregate stability experiments described above, the diffusion of

oxygen was investigated in laboratory-prepared soil cores, the solubility of oxygen was investigated in unsaturated soils and vermiculite.

GAS ANALYSIS AND OTHER MEASUREMENTS ON SOILS
HAVING ARTIFICIALLY STABILIZED AGGREGATES

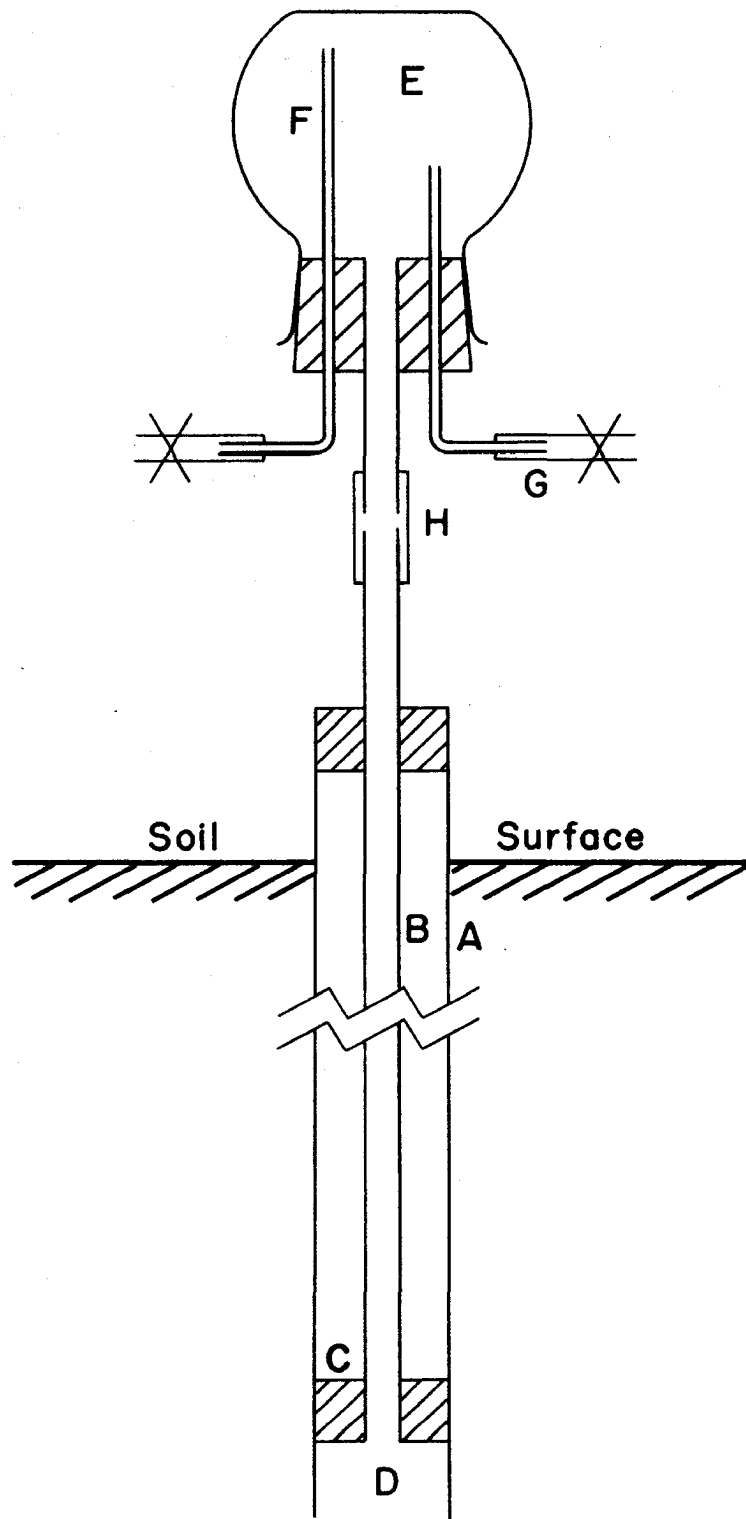
Two soil conditioner experiments were established in the fall of 1952, one on Webster silty clay loam soil located at the Agronomy Farm, Ames, Iowa, and the other on Edina silt loam soil located at the Southern Iowa Experimental Farm, Bloomfield, Iowa. Each of these experiments contained four treatments: low fertility, low fertility plus conditioner, high fertility, and high fertility plus conditioner. Each treatment was replicated four times. The experiment located on Webster silty clay loam was a randomized block design, that on Edina silt loam, a latin square design. The soil conditioner, a vinyl acetate of maleic acid (VAMA) powder supplied by the Monsanto Chemical Company, was disked into the surface 6 inches of soil at the rate of 2 tons per acre. In order to break the soil up into small aggregates, the surface 6 inches of soil was disked twice before application of the conditioner. After application, the surface was disked two times more in order that the conditioner might be thoroughly mixed with the surface soil. Although the low fertility treatments received no fertilizer application, the high fertility treatments received an application in the spring, before plowing, of 120 pounds of N, 120 pounds of P_2O_5 and 120 pounds of K_2O per acre. In the spring of 1953, corn was

planted and thinned to a population of 16,000 plants per acre. Every plot, conditioned and not-conditioned, received an application at planting time of 4 pounds of N, 16 pounds of P_2O_5 , and 8 pounds of K_2O per acre, as a starter fertilizer. Measurements, both oxygen concentration and physical properties were made throughout the growing season of 1953 on both soil conditioner experiments.

Methods and Materials

The oxygen concentrations of the field plots were obtained by placing diffusion equilibrium probes in the soil and measuring the oxygen concentration at different periods of time. A diagram of one of these probes used to measure the oxygen concentration on the conditioner experiments is shown in Figure 1. The probe, similar to that of Taylor (54), consists of an outer tube A and an inner tube B. The outer tube was constructed from 1-inch thin-wall electrical conduit, the inner tube of 1/2-inch copper pipe. To seal the inner copper pipe to the electrical conduit, a rubber stopper C was used at each end of the probe. To further strengthen the seal, melted paraffin was poured on top of the rubber stopper at the bottom of each probe. A small cavity D formed by placing the rubber stopper and the copper pipe 1 inch from the end of the electrical conduit was made on each probe.

Figure 1. A diagram of the oxygen diffusion probe
showing the essential parts (not to scale)



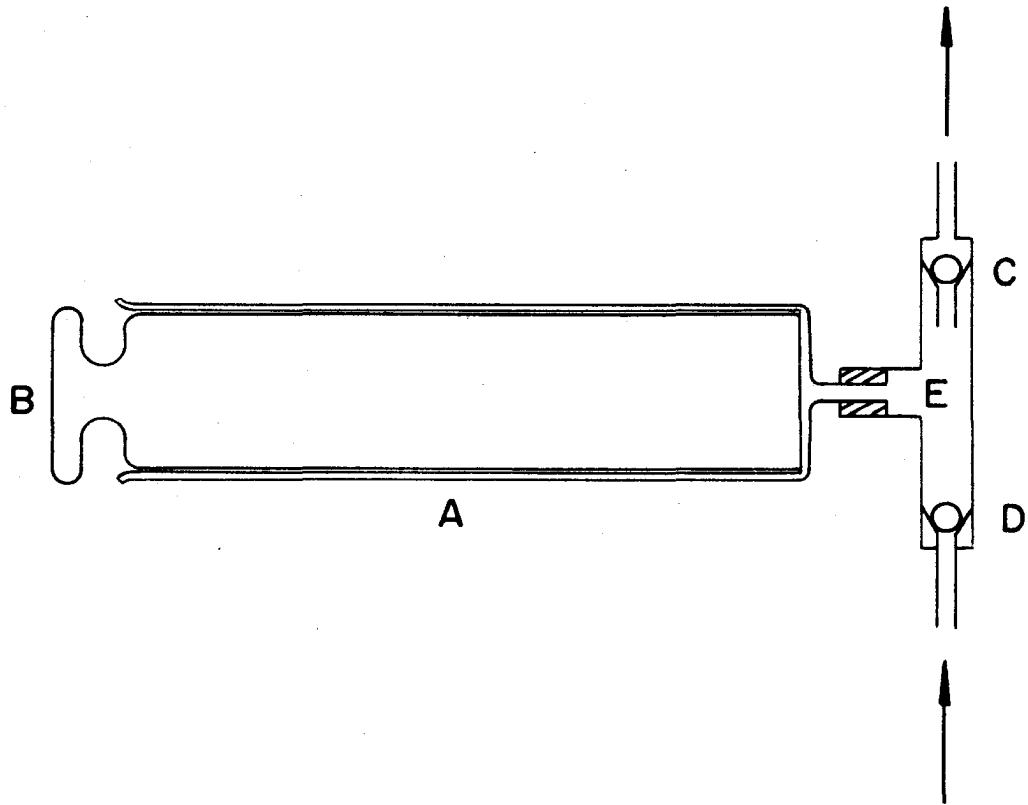
Several lengths of probes were used: 9 inches, 18 inches, 30 inches, and 42 inches. These lengths were chosen in order that 6 inches of each probe could remain above the surface of the soil while the bottom of the probes could be placed at depths of 3 inches, 1 foot, 2 feet, and 3 feet. In order that the 9-inch probe could be supported in the 3 inches of surface soil, a 6-inch horizontal brace was welded to each probe. The other lengths of probes did not need bracing as they were supported by the surrounding soil. A glass collection bottle E for obtaining soil air samples from the probe cavity was a 50 cc., wide-mouth, extraction flask, closed by a no. 6, three-holed, rubber stopper. A 1/2-inch copper pipe, like the one in the 1-inch tube, extends through the center of the rubber stopper. This copper pipe of the flask joined, by means of rubber tubing H, the 1/2-inch copper pipe of the probe. In addition, two pieces of 1/16-inch copper tubing F ran through the rubber stopper of the flask. One of these copper tubings extended to a greater distance into the collection bottle than the other to facilitate a required circulation of the gas through the probe, collection flask and an oxygen measurer (analyzer) during measurement. This circulation is done with a circulation syringe to be described. To seal the chamber E from the atmosphere, small rubber tubing G was placed on each copper pipe. To further seal this connection, a layer of stopcock grease was put between all

metal-to-rubber tubing connections and a coat of paraffin to all rubber connections and tubing.

The diffusion equilibrium probes were placed in the soil by augering out a 1-inch cavity to the desired depth. These probes, fitting tightly into the cavity, were driven to the desired depth. The surface soil was tamped around each probe. A vertical rod was pushed through, and maintained in the inner wall B of each probe, while being put in the soil. The rod was used to insure that loose soil would not clog the passage. The collection flasks were then placed on the probes. Four probes were placed in each plot at a distance of 6 inches from different corn hills and at depths of 3 inches, 1 foot, 2 feet, and 3 feet. The probes were placed in the plots about three weeks previous to the first date of measurement which was June 20 or 27.

The circulating syringe (Figure 2) was constructed from a 25 cc. syringe which had a metal connection tip. To the metal tip were soldered two metal ball seats so arranged that gas could be circulated with the syringe. The 25 cc. syringe cavity A had a ground glass connection with plunger B. Stopcock grease was used as a lubricant for plunger B. The ball seat at D was arranged so that gas could be drawn into chamber E when the plunger was pulled out. When the plunger was pushed in, the ball seat at D closed the passage from the chamber. The ball seat at C was so arranged that,

Figure 2. A diagram of the circulating syringe
showing the essential parts



when the plunger was pulled out, no gas could enter chamber E through C but, when the plunger was pushed in, the gas from chamber E would go out at the metal ball seat C. Repeated pushing and pulling of the plunger would circulate a gas through a system without introducing much volume into the system or contaminating the gas by atmospheric air.

The oxygen measurements were made with a portable Beckman oxygen analyzer, obtained from the Arnold O. Beckman Company. The analyzer actually measures the partial pressure of oxygen; however, the scale is recorded in percentage oxygen. The meter read 20% oxygen full scale for atmospheric air. The instrument was checked for the zero level by introducing pure nitrogen for which the scale reading was actually zero. The true value of the oxygen percentage should be 20.5% at the elevation of the experiments. Since it was desired to measure relative differences, the meter readings were reported directly.

The oxygen concentrations were measured by first placing the Beckman oxygen analyzer and circulation syringe near the flask of Figure 1. A photograph showing the flask (on top the pipe), Beckman oxygen analyzer, and syringe is shown in Figure 3. The Beckman analyzer was supported on a box and levelled to insure proper sensitivity.

Before measuring the oxygen concentration in the flask, atmospheric air was circulated through the Beckman oxygen

Figure 3. A photograph showing the oxygen concentration being determined in the diffusion equilibrium probes in the field



analyzer and rubber connection tubes with the circulating syringe. This filled the connecting tubing between the syringe and oxygen analyzer with gas of known atmospheric oxygen concentration. A reading of the atmospheric oxygen concentration was taken to insure that the analyzer performed properly. The rubber connection tubes from the analyzer were then connected to the rubber tubing on the probe flask at G of Figure 1 and the clamps removed from the rubber tubing. A clamp having been placed on the rubber tubing connecting the flask with the probe at H, the gas in the flask E was then circulated through the Beckman oxygen analyzer with the circulating syringe. The resulting oxygen concentration was recorded for the flask. The oxygen concentration in the flask (that is of the soil atmosphere) was corrected for the oxygen from the air in the Beckman oxygen analyzer and small rubber connecting tubing to give the true oxygen concentration of the soil.

Five aggregate samples from each plot were collected at two different dates on each soil conditioner experiment. These field samples were then passed through an 8 mm. sieve, air-dried, and stored for the laboratory aggregate analysis which was later determined by the usual Yoder technique (49).

To see how the soil moisture affected oxygen concentration, soil moisture samples were taken at different dates throughout the growing season on each of the two soil con-

ditioner experiments. For this, 16 samples were taken with a Viehmeyer type of sampling tube in each plot on the zero to 1 foot depths. Eight samples were taken from each plot at depths from 1 to 4 feet while two samples were taken at depths greater than 4 feet. The samples for each plot were composited and two subsamples were taken from the composite for laboratory determination for moisture content. The subsample for laboratory determinations was placed in moisture cans, sealed with masking tape, and transported to the laboratory for analysis. The moisture content of the samples was then determined on an oven-dry basis of 105° C.

Corn leaf samples were taken at 75% silking for potassium content of the leaves. For this phase of the experiment, the leaf below and opposite to the major ear was taken. Ten corn hills were sampled from the center of each plot with two leaves being taken from each corn hill. These leaves were oven-dried, ground, and stored for laboratory determination of potassium content. Later this plant material was dry ashed at 400° C. The ash was dissolved in dilute HNO_3 and the potassium content determined on a flame photometer which had lithium as an internal standard.

Corn yields were determined on both soil conditioner experiments by removing corn from the center two rows of each plot. An area two corn rows wide and 30 feet long was sampled from each plot. The corn was weighed, corrected for

the moisture content of the shelled corn, and expressed as corn yields in bushels per acre.

Results

Oxygen concentration measurements

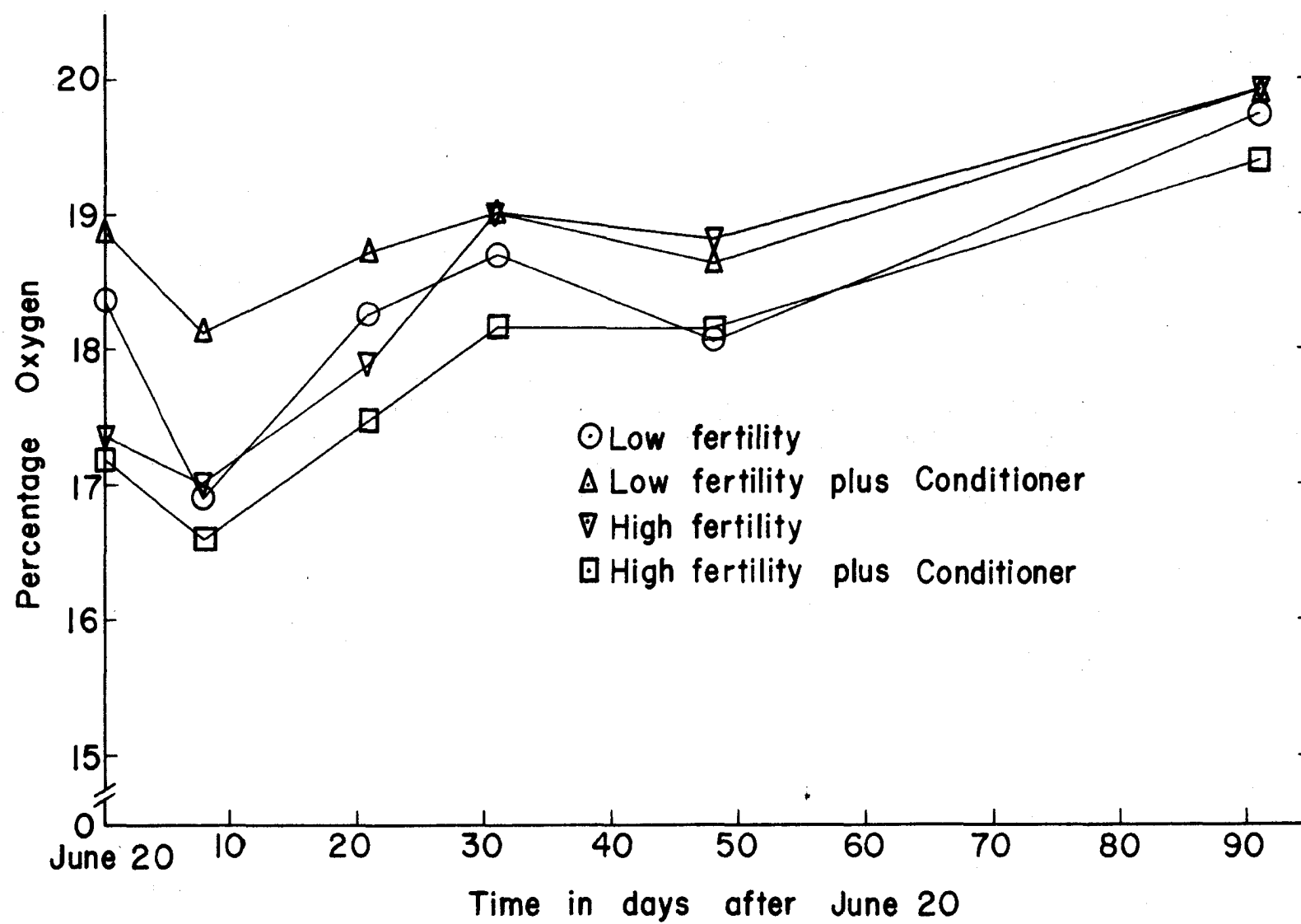
The results of the oxygen concentration measurements taken on the Webster silty clay loam soil during 1953 are shown in Table 1 where the first column gives the dates of measurements. The other columns show the oxygen concentration in the soil and range of oxygen concentration found for the different treatments. Since each oxygen concentration value reported in the table is a mean for four depths and four replications, the value gives the average oxygen status for a 3-foot depth of soil. The ranges reported are the extremes of oxygen concentration values found for individual probes at the particular date and treatment. A statistical analysis of the data at each measuring date shows that there was no statistically significant difference in oxygen concentration as a result of either fertility or conditioner treatment on any date of measurement. (By "statistically significant" is meant 0.95 probability.) The oxygen concentration values reported in Table 1 are graphed in Figure 4 in order to give a more complete picture of the oxygen concentration

Table 1. Soil oxygen concentrations in percents by volume* for the different treatments during 1953 on the soil conditioner experiment located on Webster silty clay loam

Dates	Treatments							
	<u>Low fertility</u>		<u>Low fert. + conditioner</u>		<u>High fertility</u>		<u>High fert. + conditioner</u>	
	Av.	Range	Av.	Range	Av.	Range	Av.	Range
6/20/53	18.39	14.25 to 20.00	18.89	17.25 to 20.00	17.34	8.50 to 20.00	17.20	14.75 to 20.00
6/28/53	16.89	12.25 to 19.25	18.16	16.00 to 19.50	17.00	6.75 to 19.50	16.66	12.50 to 19.50
7/12/53	18.25	16.25 to 19.50	18.75	16.75 to 20.00	17.92	6.00 to 19.50	17.47	10.25 to 19.50
7/22/53	18.70	16.75 to 20.00	19.02	17.00 to 20.00	19.05	17.75 to 20.00	18.16	10.75 to 20.00
8/ 8/53	18.08	16.25 to 20.00	18.64	17.00 to 20.00	18.78	17.25 to 20.00	18.11	9.25 to 20.00
9/19/53	19.73	17.00 to 20.00	19.92	19.25 to 20.00	19.92	18.25 to 20.00	19.40	11.00 to 20.00

*Values in the first column under each date are the average values of the 3-inch, 1-foot, 2-foot and 3-foot depths in four replications (average of 16 values).

Figure 4. Soil oxygen concentrations in percents by volume for the different treatments during 1953 on the soil conditioner experiment located on Webster silty clay loam



changes throughout the season. As the season progressed and the soil dried, the oxygen concentration in the soil increased, reaching the maximum recorded value on the last sampling date.

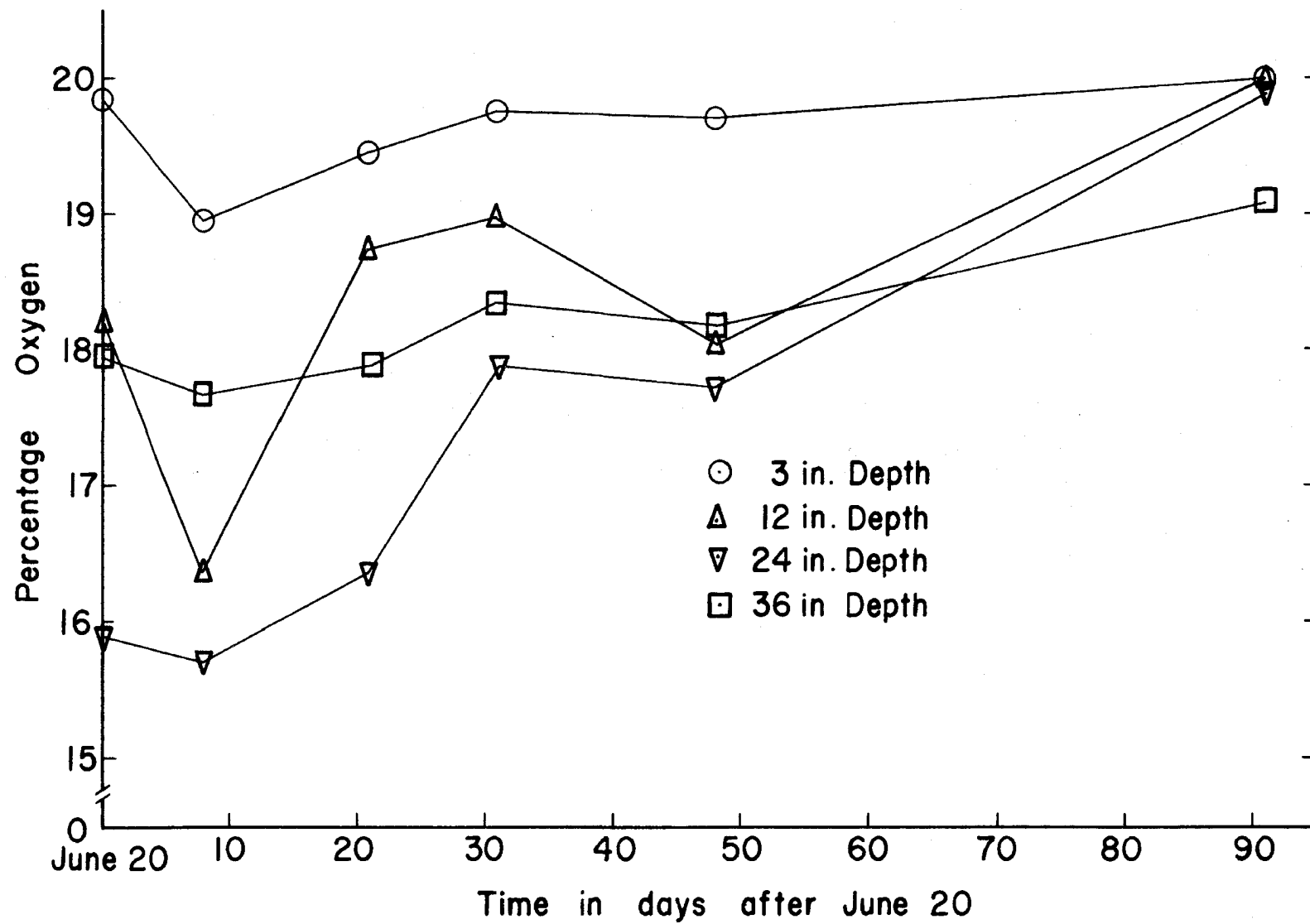
The soil oxygen concentration for the different depths on the Webster silty clay loam experiment is shown in Table 2. The first column of Table 2 gives the date of measurement. The other columns of the table give the oxygen concentration and range of oxygen concentrations at the different depths. The oxygen concentrations reported in Table 2 are the mean of the four treatments and four replications. The range of oxygen concentration reported in the table includes the extreme values observed in the 16 soil oxygen concentrations on the particular date of measurement. A statistical analysis of the data in Table 2 shows a significant difference in oxygen concentration between the different depths at all dates of samples except August 19, 1953, on which date the concentrations were all very nearly atmospheric (20.00% as given by the Beckman meter). In order to give a more complete picture of the changes in oxygen concentration for the different depths throughout the year, the data in Table 2 are graphed in Figure 5. In Figure 5, the oxygen concentrations for the different depths are plotted as a function of time throughout the growing season.

The results of the oxygen concentration measurements for the different treatments on the soil conditioner experiment

Table 2. Soil oxygen concentrations in percents by volume for the different depths during 1953 on the soil conditioner experiment located on Webster silty clay loam

Dates	Depths							
	3 in.		12 in.		24 in.		36 in.	
	Av.	Range	Av.	Range	Av.	Range	Av.	Range
6/20/53	19.84	19.50 to 20.00	18.19	8.50 to 20.00	15.88	8.50 to 18.00	17.92	13.25 to 20.00
6/28/53	18.95	18.25 to 19.50	16.38	13.50 to 18.25	15.70	6.75 to 18.75	17.67	12.00 to 19.25
7/12/53	19.44	18.25 to 20.00	18.73	18.25 to 19.00	16.34	6.00 to 19.00	17.88	10.25 to 19.50
7/22/53	19.73	19.25 to 20.00	18.97	18.75 to 19.25	17.88	16.25 to 19.25	18.34	10.75 to 19.50
8/ 8/53	19.70	19.25 to 20.00	18.03	17.00 to 19.00	17.70	16.25 to 19.00	18.17	9.25 to 20.00
9/19/53	20.00	20.00	20.00	20.00	19.89	19.25 to 20.00	19.09	11.00 to 20.00

Figure 5. Soil oxygen concentrations in percents by volume for the different depths during 1953 on the soil conditioner experiment located on Webster silty clay loam



located on Edina silt loam are shown in Table 3. The oxygen percentages in the tables are arithmetic means of 16 different equilibrium values. The range of oxygen percentages reveal the extremes found at all depths on the measurement date. A statistical analysis of the data in Table 3 at each measurement date shows no significant difference in oxygen concentration as a result of the fertility or conditioner treatment. The oxygen concentration data in Table 3 are graphed in Figure 6 to show more completely the changes that occurred during 1953. In Figure 6, the oxygen concentration is plotted at the different dates of measurement during the growing season. Each value plotted is a mean of 16 different soil oxygen concentration values.

The oxygen concentration for the different depths of measurements is summarized in Table 4 where each oxygen concentration is a mean of 16 different equilibrium values. The range of oxygen concentration reported shows the extreme values observed at the particular depth and date. A statistical analysis of the data indicates a statistically significant difference in oxygen concentration between the depths at all dates of measurement. The mean oxygen concentrations reported in Table 4 are graphed for the different measurement dates in Figure 7. In Figure 7, is shown the oxygen concentration for the different depths at the particular dates of measurements throughout the growing season.

Table 3. Soil oxygen concentrations in percents by volume* for the different treatments during 1953 on the soil conditioner experiment located on Edina silt loam

Dates	Treatments							
	<u>Low fertility</u>		<u>Low fert. + conditioner</u>		<u>High fertility</u>		<u>High fert. + conditioner</u>	
	Av.	Range	Av.	Range	Av.	Range	Av.	Range
6/27/53	18.18	12.25 to 20.00	18.31	12.00 to 20.00	18.04	13.50 to 20.00	18.34	13.75 to 20.00
7/ 2/53	18.19	12.25 to 20.00	17.97	10.75 to 20.00	17.88	12.00 to 19.50	17.94	10.75 to 19.50
7/ 3/53	18.25	13.00 to 19.50	18.14	11.00 to 20.00	18.14	12.25 to 19.50	18.16	11.25 to 20.00
7/ 4/53	18.38	13.50 to 19.50	18.36	11.00 to 20.00	18.09	13.00 to 20.00	18.17	11.50 to 20.00
7/17/53	18.34	11.50 to 19.50	18.05	7.25 to 19.50	18.39	11.50 to 19.50	18.25	9.75 to 19.50
8/ 7/53	19.13	17.25 to 20.00	19.13	17.75 to 20.00	19.19	18.25 to 20.00	19.31	16.75 to 20.00
8/31/53	19.31	17.75 to 20.00	19.28	18.00 to 20.00	19.31	18.75 to 19.50	19.38	18.75 to 20.00
9/ 9/53	19.83	17.75 to 20.00	19.88	18.00 to 20.00	19.94	19.50 to 20.00	19.94	19.50 to 20.00

*Values in the first column under each date are the average values of the 3-inch, 1-foot, 2-foot and 3-foot depths in four replications (average of 16 values).

Figure 6. Soil oxygen concentrations in percents by volume for the different treatments during 1953 on the soil conditioner experiment located on Edina silt loam

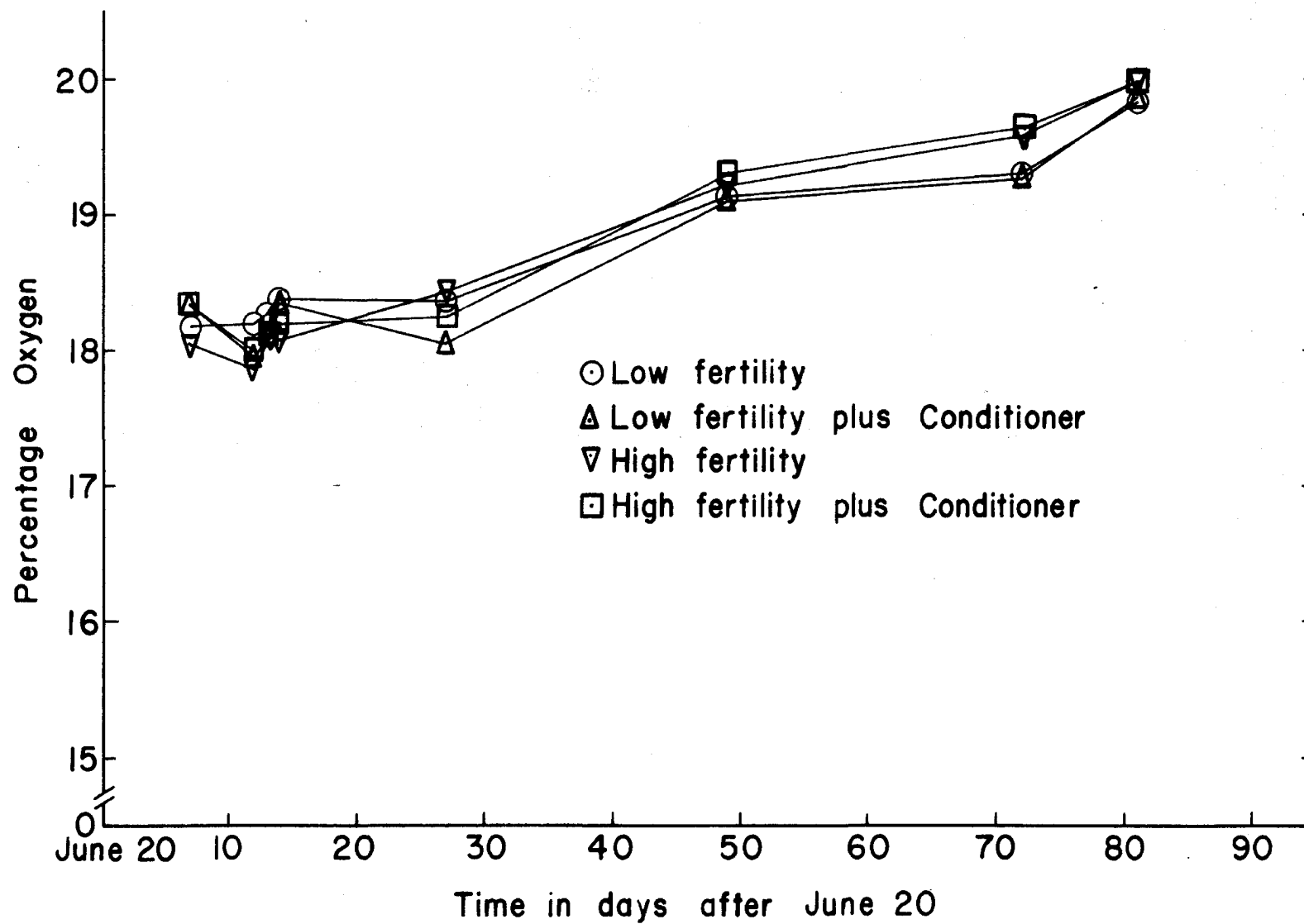
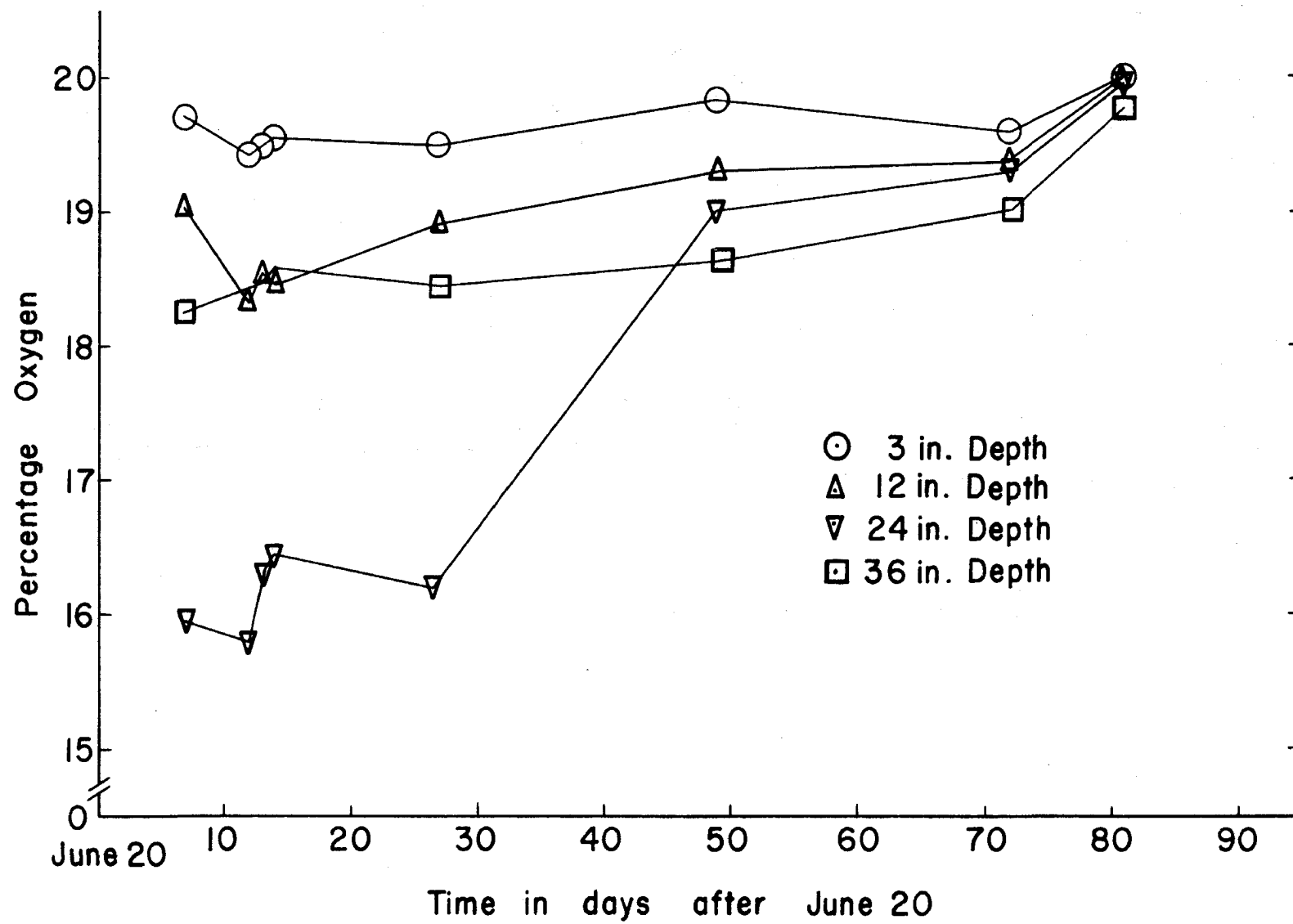


Table 4. Soil oxygen concentrations in percents by volume for the different depths during 1953 on the soil conditioner experiment located on Edina silt loam

Dates	Depths							
	3 in.		12 in.		24 in.		36 in.	
	Av.	Range	Av.	Range	Av.	Range	Av.	Range
6/27/53	19.69	18.75 to 20.00	19.03	18.00 to 20.00	15.94	12.00 to 19.25	18.23	16.75 to 19.50
7/ 2/53	19.42	18.75 to 20.00	18.33	16.00 to 20.00	15.81	10.75 to 19.25	18.41	17.25 to 19.50
7/ 3/53	19.47	18.75 to 20.00	18.51	17.25 to 19.25	16.27	11.00 to 19.50	18.44	17.25 to 19.50
7/ 4/53	19.52	19.25 to 20.00	18.47	17.75 to 19.25	16.44	11.00 to 19.25	18.58	17.00 to 19.50
7/17/53	19.47	19.25 to 19.50	18.94	18.75 to 19.25	16.19	7.25 to 19.25	18.44	16.75 to 19.50
8/ 7/53	19.81	19.50 to 20.00	19.31	19.00 to 19.50	19.00	18.75 to 20.00	18.63	16.75 to 19.50
8/31/53	19.58	19.50 to 20.00	19.38	18.75 to 20.00	19.31	19.25 to 19.50	19.02	17.75 to 19.50
9/ 9/53	20.00	20.00	20.00	20.00	19.94	19.50 to 20.00	19.77	17.75 to 20.00

Figure 7. Soil oxygen concentrations in percents by volume for the different depths during 1953 on the soil conditioner experiment located on Edina silt loam



Aggregate analysis measurements

The results of the aggregate analysis of samples collected during 1953 on both soil conditioner experiments are shown in Table 5. The data reported in Table 5 are for the percentage of aggregates greater than 2 mm. in diameter.

Each value reported in Table 5 is a mean of four replications. A statistical analysis of the aggregate analysis data on the Webster silty clay loam at each sampling date shows an increase in the percent of aggregate greater than

Table 5. The percent of aggregates greater than 2 mm. on the soil conditioner experiments located on Webster silty clay loam and Edina silt loam soils

Soil type	Treatment			
	Low fertility	Low fert. + conditioner	High fertility	High fert. + conditioner
<u>7/12/53</u>				
Webster silty clay loam	3.17	22.64	1.94	26.71
<u>10/12/53</u>				
	4.75	32.69	7.01	35.14
<u>7/ 8/53</u>				
Edina silt loam	0.98	10.26	1.05	9.78
<u>10/22/53</u>				
	4.02	9.57	3.00	7.53

2 mm. as a result of the conditioner application. This increase was significant at 0.99 probability or higher. On Edina silt loam, a statistically significant (0.95 probability) increase in the percent of aggregates greater than 2 mm. was obtained at both sampling dates. There were no significant differences in the percent of aggregation greater than 2 mm. as a result of the fertilizer application on either soil type.

Soil moisture measurements

The results of the soil moisture samples taken on the soil conditioner experiment located on Webster silty clay loam during 1953 are summarized in Table 6. Each value reported in Table 6 is a mean of four replications.

When a statistical analysis of the data reported at each sampling date was made, it was found that at no time was there a statistically significant difference in the moisture content of the plots as a result of either fertilizer or conditioner treatments. On the August 24th sampling date, there was a significant difference in the moisture contents between the different depths.

The results of the soil moisture samples taken during the 1953 growing season on the soil conditioner experiment located on Edina silt loam are shown in Table 7. Each

Table 6. Soil moisture percentages at different dates throughout 1953 on the soil conditioner experiment located on Webster silty clay loam soil

Depth (in.)	Treatment			
	Low fertility	Low fert. + conditioner	High fertility	High fert. + conditioner
<u>3/27/53</u>				
0-6	28.6	29.7	29.9	27.7
<u>4/14/53</u>				
0-6	30.8	30.9	30.3	31.8
<u>8/24/53</u>				
0-6	19.0	21.1	19.1	19.8
6-18	17.9	20.4	18.6	19.6
18-30	16.2	16.7	16.6	17.3
30-42	15.4	16.6	15.7	17.5

value reported in Table 7 is a mean of four replications.

On the April 21 sampling date, there was a statistically significant increase in the moisture percentage as a result of the conditioner application. This increase was consistent for both the 0-3 inch and 3-6 inch depths. On the contrary, a statistical analysis of the data collected on July 17 shows no significant difference in the moisture content of the plots as a result of either the conditioner or fertilizer application. There was, however, a significant interaction of treatment with depths on this particular date of sampling. A significant difference in moisture content at the different

Table 7. Soil moisture percentage on different dates throughout 1953 on the soil conditioner experiment located on Edina silt loam soil

Depth (in.)	Treatment			
	Low fertility	Low fert. + conditioner	High fertility	High fert. + conditioner
<u>4/21/53</u>				
0-3	31.6	35.4	30.8	36.9
3-6	31.7	35.7	32.5	34.9
<u>7/17/53</u>				
0-6	17.2	15.4	16.1	14.8
6-12	19.3	18.5	17.8	17.6
12-24	24.6	24.1	25.2	25.3
24-36	35.3	35.6	35.3	35.1
<u>8/31/53</u>				
0-6	7.3	6.6	7.1	6.3
6-18	13.3	12.4	13.0	13.7
18-30	23.9	23.7	23.6	23.1
30-42	24.4	23.8	23.6	22.9
<u>11/10/53</u>				
0-6	9.7	9.9	10.4	10.1
6-18	13.4	13.2	14.0	12.9
18-30	24.2	24.1	25.2	23.8
30-42	24.8	24.2	23.7	23.2
42-54	23.5	23.1	22.9	22.3
54-66	27.5	27.5	27.3	25.6
66-78	27.3	26.6	26.7	26.2
78-90	27.9	29.4	28.0	30.4

depths was also found on the July 17 sampling date. On the August 31 and November 10 sampling dates, however, there was no significant difference in moisture content of the plots as a result of either the conditioner or the fertilizer

application, but on both dates of sampling there was observed a significant difference in moisture content between the different depths.

Corn leaf analysis

The results of the potassium analysis of the corn leaves on both soil conditioner experiments are shown in Table 8. Each value reported in Table 8 is a mean of four replications.

Table 8. The percent potassium in corn leaves samples on soil conditioner experiments located on Webster silty clay loam and Edina silt loam

Soil type	Treatment			
	Low fertility	Low fert. + conditioner	High fertility	High fert. + conditioner
Webster silty clay loam	1.62	1.70	1.51	1.48
Edina silt loam	1.40	1.46	1.64	1.74

When a statistical analysis of the potassium content of each experiment was made, it was found that, on the soil conditioner experiment located on Webster silty clay loam, there was no significant difference in the potassium content of the

corn leaves as a result of either fertilizer or conditioner application. On the experiment located on Edina silt loam, there was a statistically significant increase in the potassium content of the corn leaves as a result of the fertilizer application but no significant difference as a result of the conditioner application.

Corn yields

The results of the corn yields harvested on both soil conditioner experiments are summarized in Table 9. Each value reported in Table 9 is a mean of four replications.

A statistical analysis was made on the corn yields harvested on the soil conditioner experiments in 1953. No

Table 9. Corn yields in bushels per acre on soil conditioner experiments in 1953

Soil type	Treatment			
	Low fertility	Low fert. + conditioner	High fertility	High fert. + conditioner
Webster silty clay loam	91.8	85.7	112.7	121.0
Edina silt loam	63.9	72.1	72.1	82.0

statistically significant difference was found on the experiment located on Webster silty clay loam as a result of the conditioner applications but a significant increase in corn yields was obtained as a result of the fertilizer application. A statistically significant increase in corn yields was obtained on the soil conditioner experiment located on Edina silt loam as a result of the conditioner application. A statistically significant increase in corn yield was also obtained as a result of the fertilizer application.

Discussions and Conclusions

The stability of the soil aggregates was greatly improved by the application of soil conditioner to both the Webster silty clay loam and the Edina silt loam soils, but the increase in stability of the aggregates was greater on Webster silty clay loam than on Edina silt loam. Since synthetic soil conditioners are believed to stabilize the existing soil aggregates, aggregation at the time of application becomes extremely important. The Webster silty clay loam soil is naturally a better aggregated soil than the Edina silt loam and, when the conditioner was applied, the Webster was probably in a better state of aggregation, thus resulting in a greater measured stability.

The moisture content of the surface soil of the Webster

was rather high at the beginning of the growing season but became dry by the latter part of July. It was apparent, however, that the conditioner or fertilizer applications had no effect on the moisture content of this soil. Similarly, the moisture content of the Edina soil followed the same general trend throughout the growing season as did the Webster, high at the beginning of the growing season yet dry by the first part of November. The Edina results differed from those of the Webster experiment in that the application of the soil conditioner increased the moisture content in the surface 6 inches of soil as measured on April 21. This increase can be explained by the fact that stabilizing the soil aggregates results in less dense soil which enables the latter to hold more water per unit mass of soil. The evaporation from the soil surface would be small at this time of the year so that, even though a loose soil may give rapid evaporation, the rate would still be small. By July 17, however, the soil moisture content in the surface soil on the conditioner treated plots was lower than in the untreated plots. This, it is believed, is because evaporation from the soil surface is high by this time of the year and the loose soil, caused by the application of soil conditioner, results in greater evaporation from the soil surface. This experiment indicates, then, that there was no difference in the moisture content of any depth other than that of the treated zone as a result of the conditioner

application.

The oxygen concentration on the Webster soil taken through the growing season showed no difference as a result of the conditioner or fertilizer treatment. Nevertheless, the order of magnitude of the oxygen concentrations was lower at the beginning of the growing season and increased as the season progressed. This increase in oxygen concentrations toward the end of the growing season is due largely to the decrease in moisture content during this same period. The oxygen concentration for low fertility plus conditioner tended to be higher throughout the growing season while that for the high fertility plus conditioner tended to be lowest although there was not enough difference to be statistically significant. At the beginning of the growing season, when the moisture content was high, there was more spread of the oxygen concentrations between the different treatments than at the end of the growing season when the moisture content was low. The range of oxygen values appeared to be more narrow on the low fertility treatments than on the high fertility treatments. Some individual values for the soil oxygen on the high fertility and high fertility plus conditioner were extremely low and remained low for a period of 30 days or longer. These results indicate that, even though the average for the treatments was high, there were small areas, probably isolated from the surrounding soil by blocked pores, where the oxygen

concentration was low.

The oxygen concentration at the different depths followed an interesting pattern. At the 3-inch depth, the oxygen concentration was high throughout the season while that for the 1-foot depth fluctuated more during the season than that of any other depth. The oxygen concentration for the 1-foot depth was high at the beginning of the season, dropped to its lowest value about eight days later, increased, and then stayed rather constant except for a small drop in August. The oxygen concentration was that of atmospheric air at the end of the growing season. At the 2-foot zone, the oxygen concentration was lower at the beginning of the season as compared to other depths and remained lower throughout most of the season. At the end of the growing season, the oxygen concentration became almost that of the atmospheric air. When considered alone, there appeared to be a linear decrease in oxygen concentration with increasing depth for the top 2 feet of soil. The third foot began the season with a high oxygen concentration and the concentration remained high throughout the growing season. There was a gradual increase in oxygen concentration with time towards the end of the growing season. The oxygen level at the 3-foot zone was slightly lower than the other depths at the date of the last measurement.

A wider range of oxygen concentration was observed with

increasing depth in the soil profile. Throughout the growing season, the range of oxygen concentration in the 3-inch depth was very narrow. The range of oxygen concentration at the 1-foot zone was wide at the beginning of the season, narrowed in the first part of July, and remained narrow throughout the remainder of the season. At the 2-foot zone, the range of oxygen concentrations was wide at the beginning of the growing season, narrowed the latter part of July, and remained narrow the remainder of the season. The range of oxygen concentration at the 3-foot depth remained wide throughout the growing season. The widening of the range of oxygen concentration with increasing depth indicates more heterogeneity in the oxygen concentrations with increasing depth. Because of the higher moisture content at the greater depth, regions in the soil appear to be isolated from the surrounding soil by blocking of the pores, an isolation which results in heterogeneous oxygen concentrations.

The oxygen concentration on the soil conditioner experiment located on Edina silt loam followed the general trend of that on the Webster. The level of oxygen was low at the beginning of the growing season and gradually increased to the end of the season. The level of oxygen at the end of the season was about the same for all treatments. The large spread in oxygen concentration which existed on the different treatments in the Webster was not observed on the Edina.

The range of oxygen concentration for the different treatments appeared to be wider at all measurement dates than on the Webster. There was no general trend of differences in the range of oxygen concentration for the different treatments. The range of oxygen concentration for all treatments was wide at the beginning of the season and narrowed toward the end of the season.

The oxygen content on the Edina at the different depths again followed the same general trend as the oxygen concentration in the Webster. At the beginning of the season, the oxygen concentration in the 3-inch zone was high and it remained almost that of atmospheric air throughout the season. The oxygen concentration at the 1-foot depth on June 27 was high; however, eight days later it dropped to its lowest level and gradually increased until, by the end of the season, the oxygen level was that of atmospheric air. The oxygen concentration at the 2-foot zone was low at the beginning of the season and increased only slightly until about July 17. After July 17, the oxygen level increased remarkably to a high level on August 7. The oxygen level then increased to about atmospheric air concentration at the end of the season. The 3-foot zone began the season rather high and remained high throughout the season. There was a gradual increase in concentration at this depth to the end of the season.

The range of soil oxygen concentration at the 3-inch and

the 1-foot depths was narrow throughout the growing season. At the 2-foot zone, the range of soil oxygen concentrations was wider than at any other depth. The range at this depth did not become narrow until the first part of August. The range of soil oxygen concentration at the 3-foot depth was narrower than the concentration at the 2-foot zone; however, the range was wider than that of the 3-inch or 1-foot zones.

Since it has been observed that the potassium absorption by plants is greatly influenced by the oxygen concentration in the medium in which the plants are growing, the potassium content of the corn leaves was determined. It was found that there was no statistically significant difference in the potassium content of the corn leaves on plants which were treated with soil conditioner. This was true for both the Webster and Edina soil. The potassium content of corn leaves in the soil conditioner plots tended to be higher than on the unconditioned soil on the Edina, but this difference was not statistically significant. On the Edina silt loam, an increase was obtained in the potassium content of the corn leaves from plants which had received the high fertility treatment. There was a trend for a decrease in the potassium content of the corn leaves on the high fertility treatments on Webster but this was not significant.

The corn yields taken from the conditioner experiments in 1953 show a rather high yield on the Webster as compared

to the Edina. There was no increase or decrease in corn yields on the Webster as a result of stabilizing the soil aggregates in the surface 6 inches of soil. An expected increase in yields as a result of the high fertility treatment was obtained on the Webster. It is important to note that the highest yields were obtained on the high fertility plus conditioner treatment on this experiment. An increase in corn yields of about 10 bushels per acre resulted from the conditioner application on the Edina silt loam. There was also an increase in corn yield as a result of the fertilizer application. The increase in corn yields as a result of the conditioner application could not be explained by any of the oxygen concentration measurements or by the potassium content of corn leaves. The only other measurement which was reflected in corn yields was aggregate analysis. The aggregates on the conditioner treated plots were more stable and the yields on these plots higher. There was, however, a trend for an increase in the potassium content of corn leaves as a result of the conditioner application. The increase in moisture content of the conditioner plots at the beginning of the season could have assisted in making available more moisture for the plant for the initial stages of growth but this was possibly not enough to last the plant any length of time as indicated by moisture measurements at later sampling dates. It is believed that the increase in corn yields on the

Edina silt loam and the trend for an increase on the Webster are results of improving the environment of the roots as a result of stabilizing the soil aggregates, but the specific aspect of the increased water stability (moisture, oxygen, etc.) associated with increased plant growth was not measured.

It has been concluded, therefore, that improving the stability of the surface 6 inches of soil, has little effect on the oxygen composition of the soil atmosphere either in the surface soil or the subsoil. The aggregate stability and the physical properties of the surface soil of Webster silty clay loam and of Edina silt loam as they exist in the field appear to be adequate for the diffusion of oxygen. If the measurements had been made in a year of high soil moisture content, the results might have been quite different.

The depth distribution of the oxygen concentration in the soils varied from that of Boynton (8) in that the oxygen concentration did not decrease linearly with increasing depth. The results obtained on Edina silt loam and Webster silty clay loam are in agreement, however, with those of Furr and Aldrich (21). Since the oxygen concentration in the soil atmosphere at the 3-foot depth was high throughout the year, it seems that there was no appreciable microbial consumption of oxygen at this depth. This was consistent for both the Webster silty clay loam and Edina silt loam. It appears that the oxygen concentration decreases in the zone where microbial

consumption takes place, that is, in the 1- and 2-foot zone. Microbial consumption undoubtedly takes place in the surface 6 inches but the diffusion impedance is so small in this zone that the oxygen concentration does not decrease.

The oxygen concentration in field soils appears to follow a cycle throughout the year. The oxygen concentration is low at the beginning of the year when the soil moisture content is high; however, as the moisture content decreases toward the end of the season, the oxygen concentration increases.

DIFFUSION AND CONSUMPTION OF OXYGEN IN SOIL CORES

Theoretical Considerations

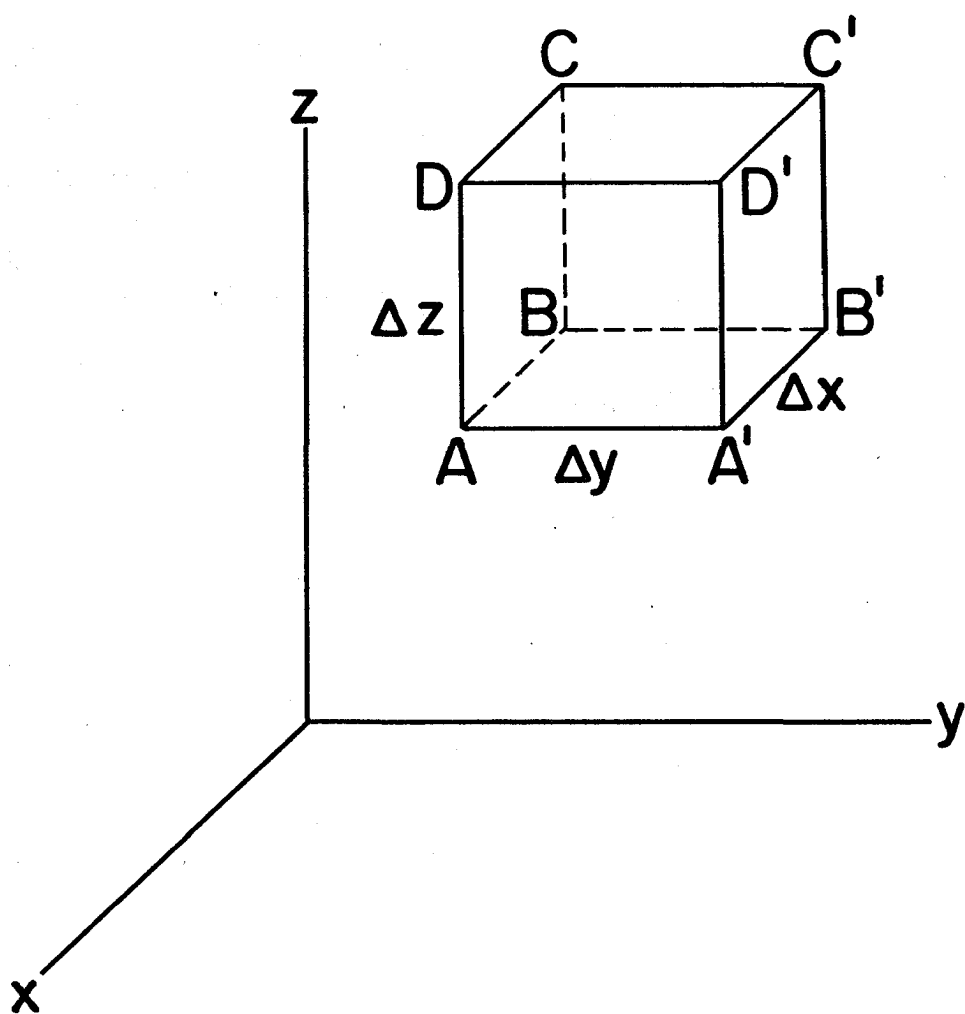
The differential equation for the diffusion of a gas through soil when evolution or consumption of the gas takes place simultaneously within the soil is developed by considering the volume element shown in Figure 8. The volume element contains the solid soil particles, the soil water, and the gas filled soil pores. The element is in the form of a parallelepiped with faces parallel to the xy , xz , and yz planes. Let $A'B' = D'C' = \Delta x$, $AA' = BB' = \Delta y$, and $AD = BC = \Delta z$. In the development of diffusion equations care must be observed in use of units.

Let the quantity (mass) of gas diffusing in the x direction into face $BB'C'C$ per unit area per unit time be q_x . Then the mass of gas diffusing into face $BB'C'C$ is $q_x \Delta y \Delta z$. At face $AA'D'D$ the mass of gas diffusing out is $[q_x + (\partial q_x / \partial x) \Delta x] \Delta y \Delta z$. The excess of mass inflow over outflow for the x direction is

$$q_x \Delta y \Delta z - [q_x + (\partial q_x / \partial x) \Delta x] \Delta y \Delta z = -(\partial q_x / \partial x) \Delta x \Delta y \Delta z .$$

Similarly the excess of mass inflow over outflow for the y direction is $-(\partial q_y / \partial y) \Delta x \Delta y \Delta z$; and the excess of mass over outflow for the z direction is $-(\partial q_z / \partial z) \Delta x \Delta y \Delta z$. Therefore the excess of mass inflow over outflow (in a unit

Figure 8. A volume element taken within a soil mass



time) for all three directions is

$$- [\partial q_x / \partial x + \partial q_y / \partial y + \partial q_z / \partial z] \Delta x \Delta y \Delta z .$$

Let gas be generated at the rate G grams per unit volume per unit time in the volume element. Then the mass of gas generated in the volume element $\Delta x \Delta y \Delta z$ per unit time is $G \Delta x \Delta y \Delta z$ and the total mass of gas accumulated per unit time in the volume element is

$$- [\partial q_x / \partial x + \partial q_y / \partial y + \partial q_z / \partial z] \Delta x \Delta y \Delta z + G \Delta x \Delta y \Delta z .$$

But if γ is the density (mass per unit volume) of gas at any instant in the volume element, and f is the fraction of the volume element which is not occupied by solid material or water, then the rate of increase of gas in the volume element may be expressed also as

$$\partial(f\gamma \Delta x \Delta y \Delta z) / \partial t = f \Delta x \Delta y \Delta z \partial\gamma / \partial t$$

where the right side is justified because f is not assumed to change with time and the size of the volume element does not. The symbol f is generally called the porosity and is dimensionless.

Equating then the two expressions for the rate of accumulation of gas in the volume element and cancelling out the factor $\Delta x \Delta y \Delta z$ one has

$$- (\partial q_x / \partial x + \partial q_y / \partial y + \partial q_z / \partial z) + G = f \partial\gamma / \partial t .$$

In experiments reported here gas is consumed rather than generated and it is therefore convenient to let G' be the rate at which gas is consumed (mass per unit volume per unit

time) and to write the above equation as

$$- (\partial q_x / \partial x + \partial q_y / \partial y + \partial q_z / \partial z) - G' = f \partial \gamma / \partial t . \quad (1)$$

If we restrict our consideration to diffusion in only one dimension, equation (1) becomes

$$- \partial q_x / \partial x - G' = f \partial \gamma / \partial t . \quad (2)$$

But Fick's first law is

$$q = - D \partial c / \partial x \quad (3)$$

whence

$$\partial q / \partial x = - D \partial^2 c / \partial x^2 \quad (4)$$

where D is the diffusion coefficient in units of length squared divided by time (L^2/t), c is concentration in mass per unit volume (M/L^3), and q is mass per unit area per unit time (M/L^2t). Substitution of (4) in (2) gives

$$f \partial \gamma / \partial t = D \partial^2 c / \partial x^2 - G' \quad (5)$$

also

$$dp = kdc$$

where p is the partial pressure; whence

$$\partial p / \partial x = k \partial c / \partial x \quad (6)$$

and

$$\partial^2 c / \partial x^2 = (1/k) \partial^2 p / \partial x^2 \quad (7)$$

where k is a constant having the units of p/c , that is of units L^2/t^2 . Substitution of (7) into (5) gives

$$f \partial \gamma / \partial t = (D/k) \partial^2 p / \partial x^2 - G' . \quad (8)$$

In the steady state condition, $\partial \gamma / \partial t = 0$, equation (8) becomes, using now total differentials rather than

partials,

$$d^2p/dx^2 = kG'/D . \quad (9)$$

Integration of (9) gives

$$p = (G'k/2D)x^2 + Ax + B \quad (10)$$

where p is the partial pressure of the gas in the soil at a distance x from a reference plane and A and B are integration constants.

Now consider a cylinder of soil with one face, $x = 0$, maintained at atmospheric partial pressure of gas P_0 and the other face exposed to a closed volume at partial pressure of gas P . Also the gas is consumed within the volume of soil by the microorganisms. Substitution of these boundary conditions into equation (10) gives

$$p = (G'k/2D)x^2 + [(P - P_0 - G'kL^2/2D)/L]x + P_0 . \quad (11)$$

From (3) and (6)

$$q = - (D/k) \partial p / \partial x$$

or in the steady state

$$q = - (D/k) dp/dx . \quad (12)$$

From (11)

$$dp/dx = (G'k/D)x + (P - P_0)/L - G'kL/2D . \quad (13)$$

Therefore in view of (12) and (13)

$$q = - G'x - (D/kL)(P - P_0) + G'L/2 . \quad (14)$$

Equation (14) yields at $x = L$ the result

$$q = - (G'L/2) - (D/k)(P - P_0)/L . \quad (15)$$

Equation (14) gives the mass of gas passing per unit area

per unit time at any distance x in the cylinder of soil. At the end $x = L$ of the cylinder of soil exposed to the closed volume, equation (15) gives the mass of gas per unit area per unit time diffusing into the closed volume.

Since $q = dQ/dt$, where Q is the quantity (mass) of gas per unit area, equation (15) becomes

$$dQ/dt = (D/k)(P_0 - P)/L - G'L/2 . \quad (16)$$

Equation (16) gives the mass of gas diffusing out of the cylinder of soil into the closed volume. This mass of gas gives a corresponding increase in partial pressure of the gas in this closed volume. Therefore

$$dQ = cdp$$

and

$$dQ/dt = cdp/dt .$$

Then equation (16) becomes

$$dp/dt = (D/ck)(P_0 - P)/L - G'L/2c \quad (17)$$

where c is a constant depending on the size of the closed volume and having the units of t^2/L . Equation (17) may be integrated as follows

$$- \int_0^P dp/(P_0 - P - b) = D/ckL \int_0^t dt$$

where

$$b = G'Lk/2D \quad (18)$$

or

$$\ln(P_0 - b)/(P_0 - P - b) = (D/ckL)t . \quad (19)$$

Changing to logarithms to the base ten, and introducing a constant d for the screen in the instrument used to hold the soil in place, equation (19) becomes

$$\log(P_0 - b)/(P_0 - P - b) = (Dd/2.303ckL)/t . \quad (20)$$

For the case when no consumption of oxygen is involved in the soil, equation (17) becomes

$$dp/dt = (D/ck)(P_0 - P)/L . \quad (21)$$

Equation (21) may be integrated similarly to equation (17) above and results in

$$\ln P_0/(P_0 - P) = (D/ckL)t . \quad (22)$$

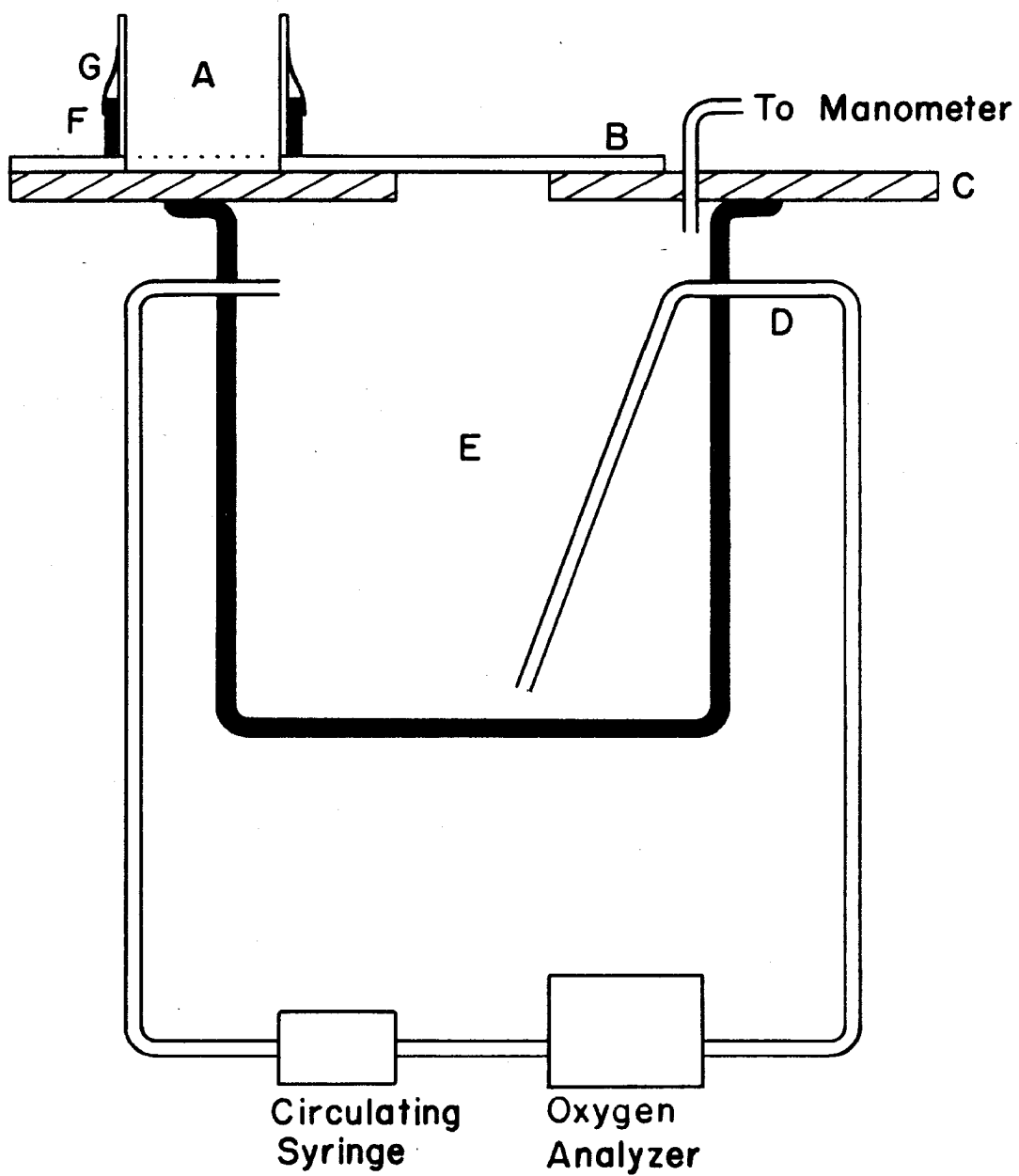
Changing to logarithms to the base ten and introducing the instrument constant d , equation (22) becomes

$$\log P_0/(P_0 - P) = (Dd/2.303ckL)t . \quad (23)$$

Methods

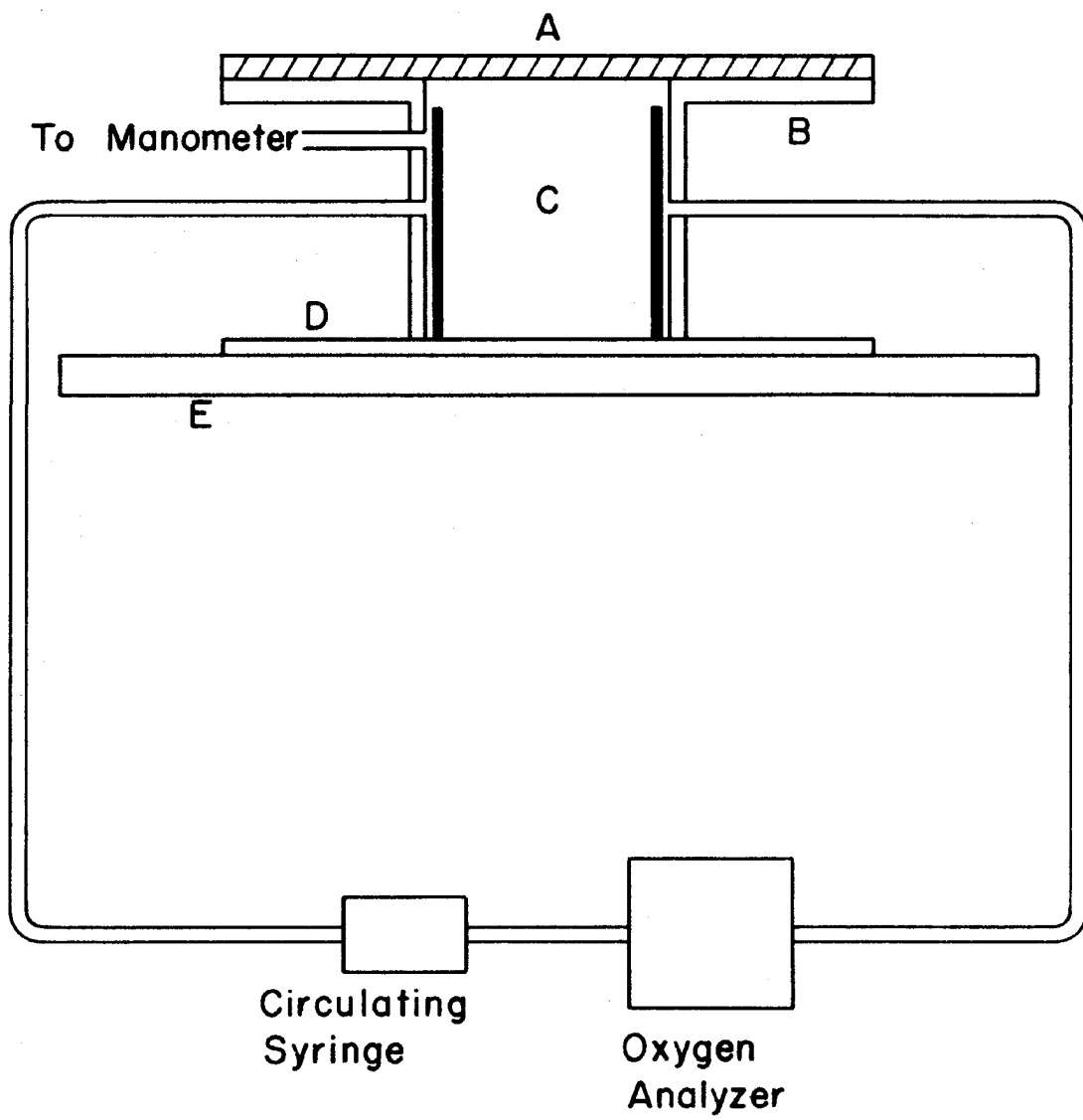
The apparatus used in the laboratory to study the diffusion of oxygen through the treated soil cores at the various tensions is shown in Figure 9. A principal component is a chamber E of volume 1370 ml. and having a ground glass base. The chamber was made from a dessicator and was sealed by stopcock grease at its ground glass surface to a brass plate C. To serve as an opening for diffusion into the chamber, a circle 1 3/4 inch in diameter was cut out of the center of brass plate C. A 1/8-inch brass plate B supported the

Figure 9. A diagram of the diffusion chamber showing
the essential parts (not to scale)



soil core by means of a flange F and Gooch rubber tubing G. The plate B was ground with carborundum so as to slide flatly on brass plate C. Petrolatum was used as a seal and lubricant between brass plates B and C. A circle of 1 3/4-inch diameter was cut out of the brass plate B and this circle aligned with the circle in brass plate C. Brass plate B was constructed so that the opening in brass plate C could be closed from the atmosphere or aligned with the opening in the brass plate B. A brass wire screen was soldered over the top of the center hole in brass plate B. The soil core A fit directly over the center opening and screen in brass plate B. The chamber apparatus was completely air tight so that, when the soil core was directly over the opening in plate C, the oxygen that entered chamber E would diffuse through the soil core. Atmospheric pressure was maintained in the chamber by means of a manometer. When the chamber E was closed, the chamber gases could be circulated through the Beckman oxygen analyzer and through the circulating syringe without contamination of the chamber gases from the atmosphere.

A diagram of the apparatus used to test the effectiveness of the phenol and sucrose solution on oxygen consumption is shown in Figure 10. The oxygen consumption apparatus consisted basically of a cylindrical brass chamber connected to an oxygen analyzer. The brass chamber C is 2 1/16 inches



in diameter and $1 \frac{3}{4}$ inches high and contains a soil core. The soil core is contained in a brass cylinder whose walls are indicated by the two heavy black vertical lines in the figure. The brass cylinder containing the soil core fits loosely in the chamber so that oxygen can circulate above and around it. The base D of the cylindrical chamber is a flat brass plate $\frac{1}{4}$ inch thick soldered to the cylinder, the plate then being bolted to a heavy wooden board E for support. A brass flange B $\frac{1}{4}$ inch thick was soldered to the top of the cylinder. A $\frac{1}{4}$ inch thick piece of plexiglas A resting on the flange B served as a top for the cylinder. Stopcock grease was used as a seal between the brass plate and the plexiglas. By means of "C" clamps, the plexiglas was fastened to brass plate B. The cylinder had two connections for circulating the gas in the closed cylinder through the Beckman oxygen analyzer. In order to maintain atmospheric pressure in the chamber, a manometer was connected to the cylinder. A circulating syringe as shown in Figure 2 was used to circulate the cylinder gases through the Beckman oxygen analyzer.

The Beckman oxygen analyzer used in the diffusion measurements had an atmospheric oxygen percentage reading of 20.75% and a pure nitrogen reading of -0.25%. These readings corresponded to a partial pressure of oxygen of 156.4 mm. for atmospheric air and 0.0 for pure nitrogen. A calibration curve was drawn for the meter readings and the true partial

pressure of oxygen. With this curve, the meter readings were converted to partial pressure readings.

Webster silty clay loam soil was collected in the field, air dried, and passed through an 8 mm. screen. The air-dry soil was stored from the time of preparation until time of use in the laboratory. Soil aggregates between 2 to 1 mm. in diameter were taken from the screened soil for laboratory use.

The 2 to 1 mm. aggregates of the Webster silty clay loam were packed into brass cylinders of 1 3/4 inches inside diameter, 1 7/8 inches outside diameter and 1 1/2 inches high. The soil was packed into the brass cylinders to a constant bulk density of 1.1 gm./cc. with the aid of an electrical vibrator.

The soil cores were saturated from the bottom with a treatment solution and placed on a tension plate or pressure plate apparatus depending upon the desired tension. The soil cores remained on the tension apparatus for a period of 48 hours. After 48 hours, the soil cores were placed on the diffusion apparatus for measurement of diffusion through them and then in the consumption apparatus for measurements of consumption.

For each tension, eight soil cores were prepared by the procedure above. Four of the cores were saturated from the bottom with 1% sucrose solution, and four of the cores were saturated with 15% phenol solution. The sucrose solution was

added to stimulate the microbial activity in the soil cores and the phenol solution was used to prevent microbial activity in the soil cores. In unpublished data at Iowa State College, it has been found that 15% phenol solution retards microbial consumption of oxygen for short periods of time.

As shown in Figure 9, the treated soil cores were placed on the plate B when the chamber E was in its closed position. A source of nitrogen was now supplied at D between the chamber and the oxygen analyzer, and nitrogen was circulated through the chamber and analyzer until the oxygen concentration in the chamber and analyzer was zero. The source of nitrogen was now disconnected and the plate B was moved to a position where the soil core was directly over the center opening in plate C. The oxygen was allowed to diffuse through the soil core into chamber E for a period of 5 minutes. Brass plate B was then moved to a position which closed chamber E and the chamber gas circulated through the Beckman oxygen analyzer until a steady value was reached. This usually required about 20 pumps on the circulating syringe. The manometer was adjusted to bring the gas in chamber E to atmospheric pressure. The oxygen concentration of the chamber gas was recorded. This process was repeated until a total diffusion time of 30 minutes was reached.

After oxygen was allowed to diffuse through the soil cores, the latter were placed in the consumption apparatus

to determine if consumption was involved in the phenol and sucrose treated cores. The soil cores were placed in the consumption apparatus and the plastic lid clamped to the apparatus. The total pressure was adjusted to atmospheric pressure with the manometer. The gas in cylinder C of Figure 10 was then circulated through the Beckman oxygen analyzer to measure the oxygen concentration at the beginning. The oxygen concentration was measured every 30 minutes for a period of two hours. The cores were then removed from the apparatus.

Results

The results of the diffusion of oxygen through laboratory prepared soil cores at the various tensions (10, 50, 100, and 300 cm. of water and 1 atmosphere) are shown in Table 10.

Each value reported in the table is a mean of four replications. A statistical analysis of the partial pressure of oxygen in the chamber at 30 minutes time was made for the different tensions. It was found that there was a significantly lower partial pressure of oxygen in the chamber at 50, 100, and 300 cm. tensions for the sucrose treated cores as compared to the phenol treated cores. It is important to note also in the table that the partial pressure of oxygen increases for both phenol and sucrose treated cores as the tension increases. This is a result of increasing the volume

Table 10. Partial pressure of oxygen in mm. of mercury in diffusion chamber for different treatments, intervals of time, and tensions of water

Treatments	Tension	Time (minutes)					
		5	10	15	20	25	30
Phenol	10 cm.	0	0	0	0	0	0
Sucrose	10 cm.	0	0	0	0	0	0
Phenol	50 cm.	0	1.1	2.0	3.4	4.8	6.3
Sucrose	50 cm.	0	0.9	1.8	2.3	3.2	4.1
Phenol	100 cm.	1.8	4.3	6.3	8.4	11.6	13.6
Sucrose	100 cm.	1.4	2.9	5.0	7.0	9.1	10.9
Phenol	300 cm.	2.3	6.1	9.7	12.5	16.1	18.8
Sucrose	300 cm.	2.0	5.2	8.4	11.8	14.5	17.4
Phenol	1 Atm.	3.2	6.8	11.3	15.4	19.0	22.7
Sucrose	1 Atm.	2.3	5.9	10.4	15.2	17.9	22.7

of air filled pores in the soil as the water tension increases.

A plot of the data in Table 10 was made using equation (23), $\log P_0/(P_0 - P)$ vs t , for both phenol and sucrose treated cores. In this plot it is remembered that P_0 is the partial pressure of oxygen in atmospheric air (156.4 mm.). The results of the plots of $\log P_0/(P_0 - P)$ vs t for the different water tensions are shown in Figures 11-15.

Regression lines were calculated for the plots of

Figure 11. The diffusion of oxygen through laboratory prepared soil cores treated with phenol solution or sucrose solution at a soil moisture tension of 10 cm. of water

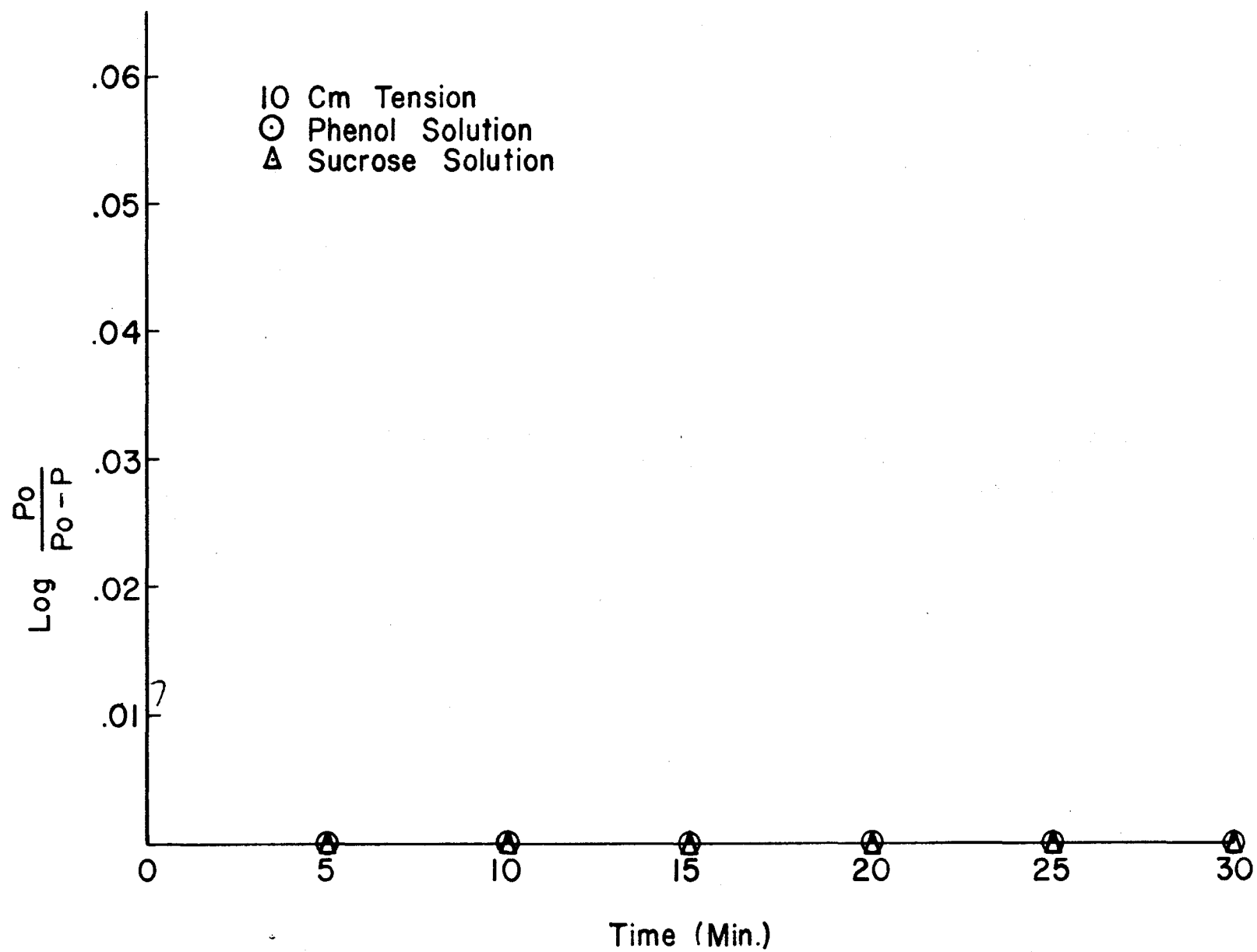


Figure 12. The diffusion of oxygen through laboratory prepared soil cores treated with phenol solution or sucrose solution at a soil moisture tension of 50 cm. of water

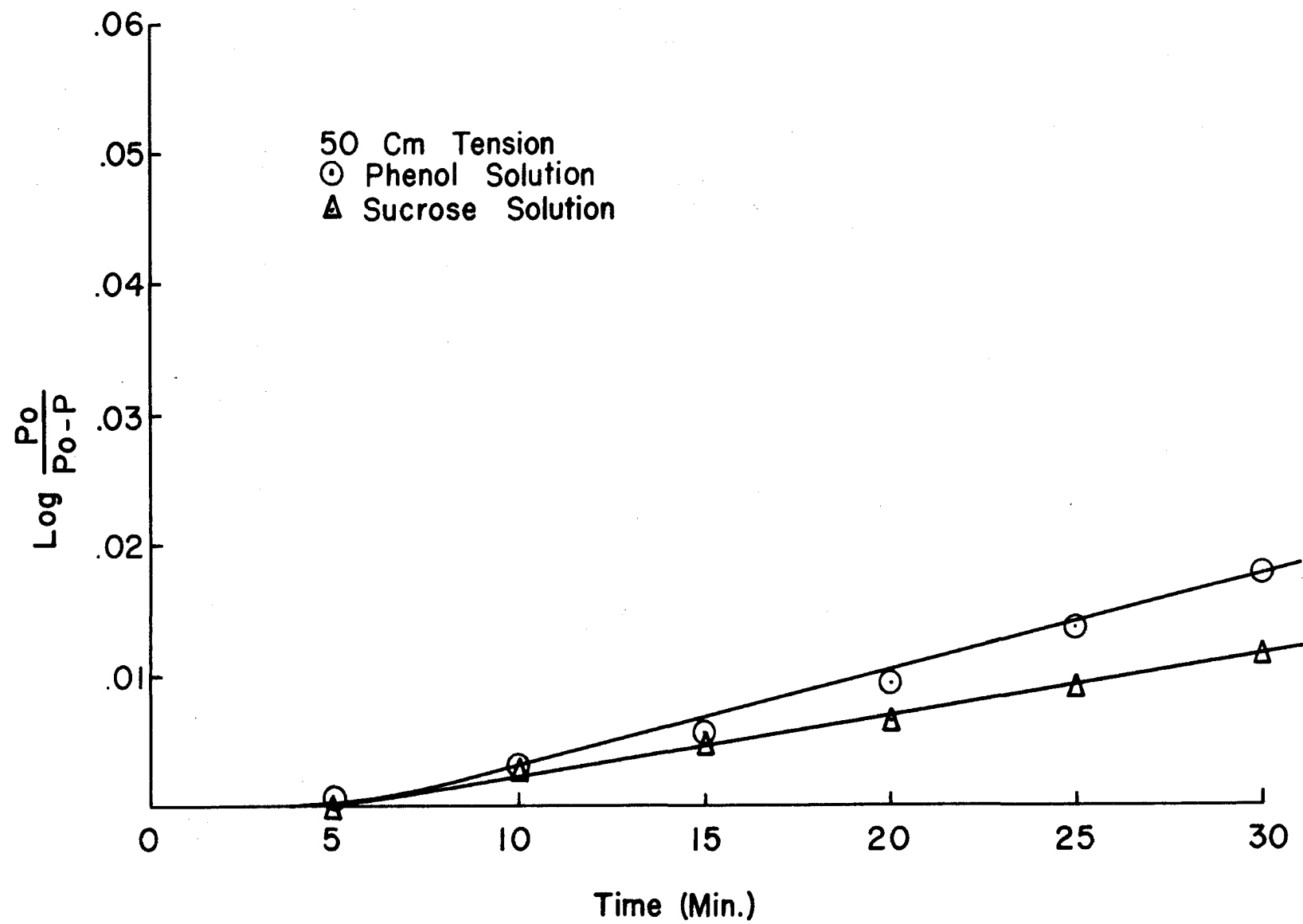
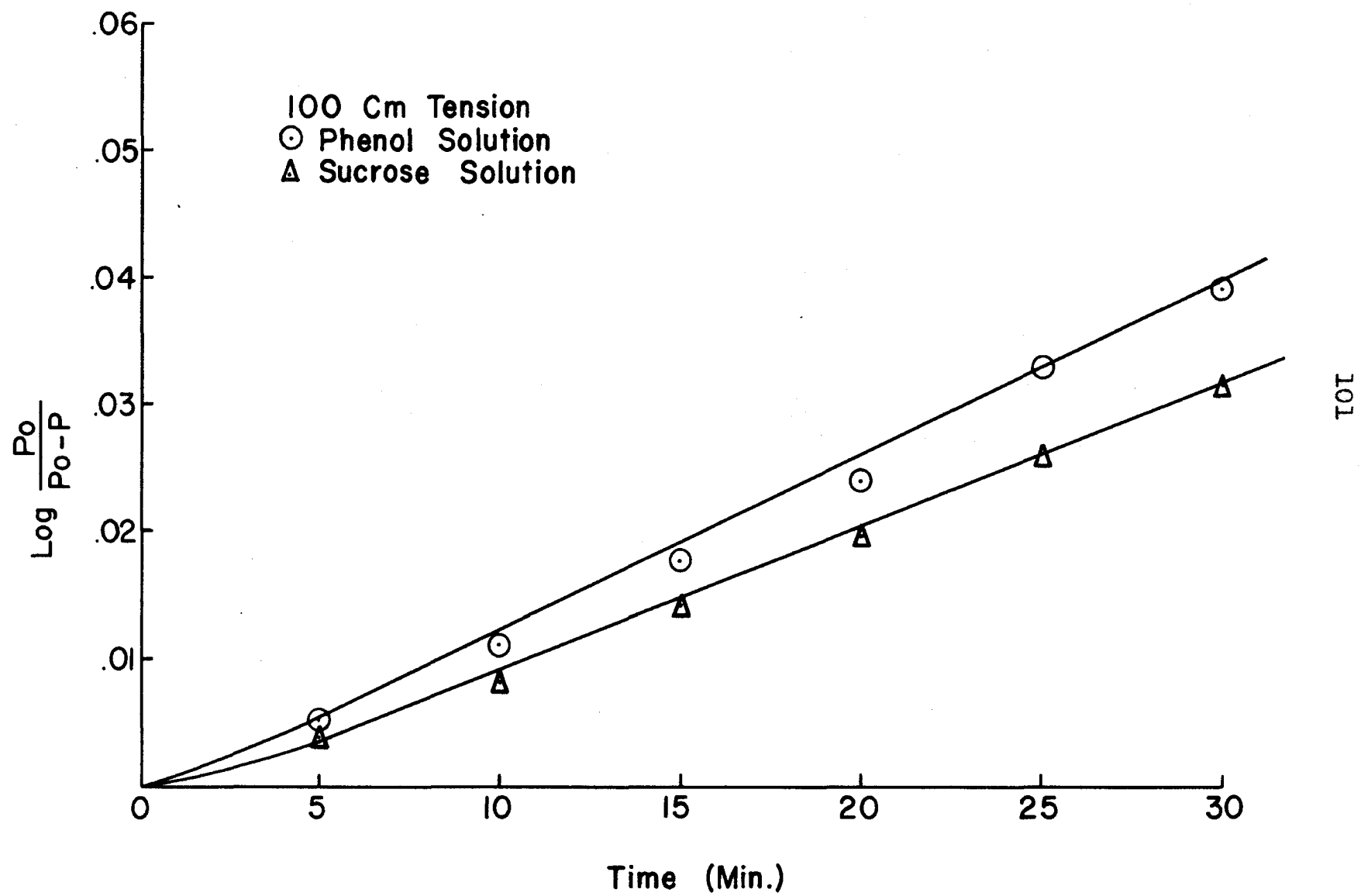


Figure 13. The diffusion of oxygen through laboratory prepared soil cores treated with phenol solution or sucrose solution at a soil moisture tension of 100 cm. of water



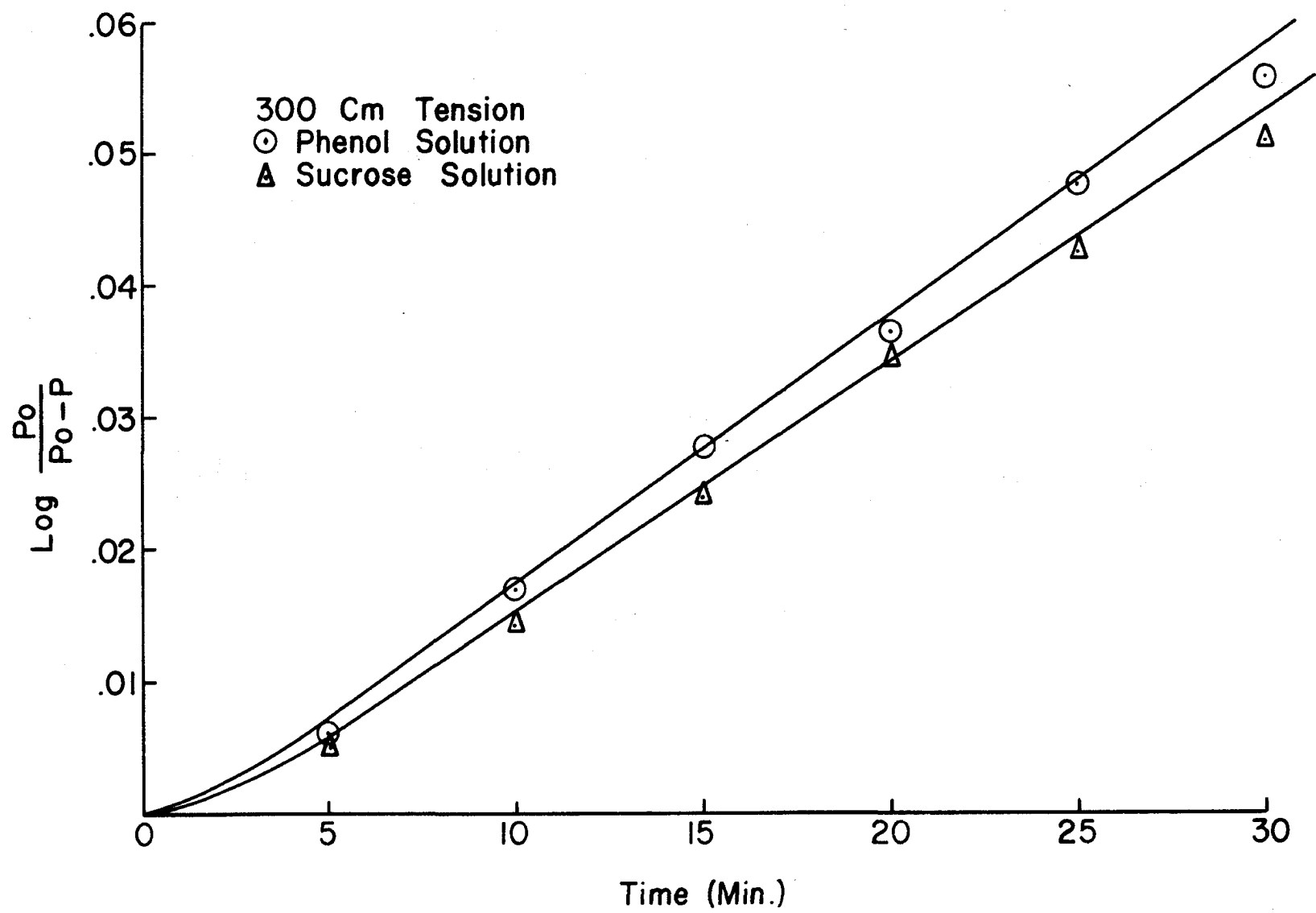
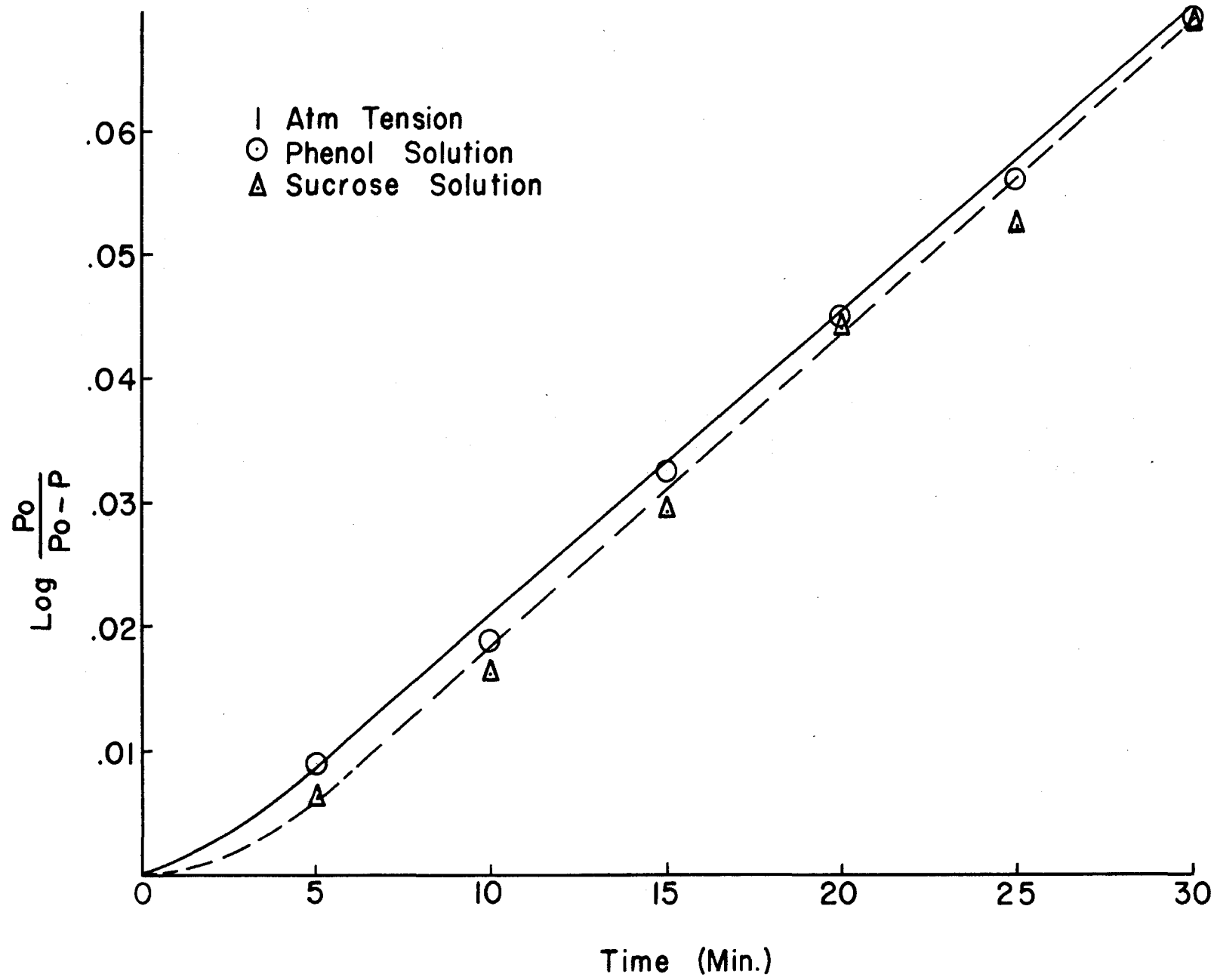


Figure 15. The diffusion of oxygen through laboratory prepared soil cores treated with phenol solution or sucrose solution at a soil moisture tension of 1 Atm. of water



$\log P_0/(P_0 - P)$ vs t for the different treatments and tensions. These lines are given in Table 11. In this table it is apparent that the lines do not go through the origin. This is probably due to the lack of establishing a steady state in the experimental procedure. In an experimental procedure for

Table 11. Regression lines for the plots of $\log P_0/(P_0 - P)$ vs t for the different treatments and tensions

Treatment	Tension	Regression line*
Phenol	50 cm.	$y = -0.00424 + 0.000715x$
Sucrose	50 cm.	$y = -0.00203 + 0.000448x$
Phenol	100 cm.	$y = -0.00212 + 0.00137x$
Sucrose	100 cm.	$y = -0.00245 + 0.00113x$
Phenol	300 cm.	$y = -0.00287 + 0.00198x$
Sucrose	300 cm.	$y = -0.00345 + 0.00183x$
Phenol	1 Atm.	$y = -0.00345 + 0.00238x$
Sucrose	1 Atm.	$y = -0.00664 + 0.00245x$

* $y = \log P_0/(P_0 - P)$ and $x = t$

the study of diffusion, one is able to obtain only an approximate steady state. The partial pressure of oxygen in the closed volume continues to increase as oxygen diffuses into the chamber during the time interval of measurement. Another reason the lines do not go through the origin is undoubtedly the failure to take the consumption coefficient b (equation

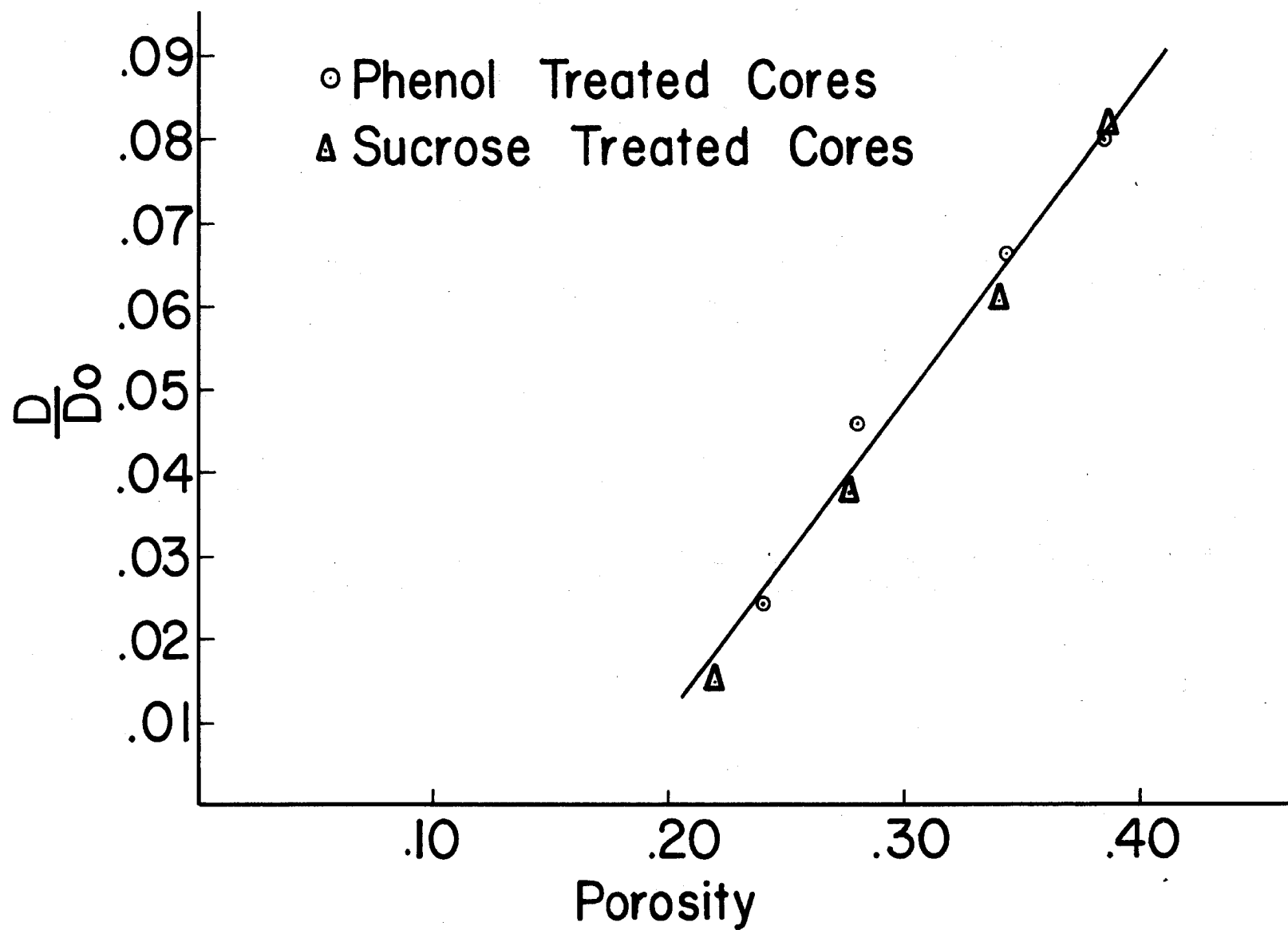
(18)) into account. A plot of the left hand side of equation (19) versus t should yield a straight line passing through the origin - not the left hand side of equation (23) - for steady state conditions.

It is apparent from Table 11 and Figures 11-15 that the slopes of the lines are greater for the phenol treated cores than the sucrose treated cores. The explanation for this will be given later.

The diffusion coefficient, D_0 , for the system was determined when no soil was in the core. The regression line for a plot of $\log P_0/(P_0 - P)$ vs t for the system when there was no soil in the core was found to be $y = 0.0923 + 0.0296x$, where $y = \log P_0/(P_0 - P)$ and $x = t$. The slope of this line (0.0296) was divided into the slopes of the lines in Table 10 for the phenol and sucrose treated cores. The resulting ratio of D/D_0 was plotted as a function of porosity in Figure 16. From Figure 16, it is apparent that a good relationship exists between porosity and D/D_0 . The plot has an intercept of zero D/D_0 at about 17% porosity. This is undoubtedly due to blocked pores which contributed to the porosity but not to diffusion.

The hypothesis that the soil microorganisms in the phenol treated cores consumed no oxygen and that soil microorganisms in the sucrose treated cores consumed oxygen was tested by placing the cores in a closed consumption chamber described

Figure 16. A plot of D/D_0 as a function of porosity for phenol and sucrose treated laboratory prepared soil cores



previously. The results of the oxygen consumption data are shown in Table 12.

Each value reported in the table is a mean of two cores. The number of cc. of oxygen given in the table was calculated from the percent of oxygen in the chamber multiplied by the volume of air space in the chamber. The volume of air space in the chamber was calculated by taking the volume of the chamber and subtracting the volume of the core itself, and the volume of soil and water in the core. The volume of the chamber was found to be 95.82 cm.³, and the volume of the core itself was 8.68 cm.³. The volumes of the soil and water in the core at the different tensions are given in column 3 of Table 12.

From Table 12, it is apparent that essentially no oxygen was consumed by the soil microorganisms in the phenol treated cores and that oxygen was consumed by the soil microorganisms in the sucrose treated cores.

The results of the porosity data on the cores given in Table 10 are shown in Table 13. Each value reported is a mean of four replications. A small but statistically significant, lower aeration porosity was obtained on the cores saturated with 1% sucrose solution as compared to cores flooded with 15% phenol solution at tensions of 10, 50, and 100 cm. of water. This indicates that at 10, 50, and 100 cm. of water tensions, the phenol treated cores had a

Table 12. The percentage and volume of oxygen in soil consumption chamber for different treatments and intervals of time

Treatment	Tension	Volume of soil & water in core (cc.)	Time (minutes)									
			0		30		60		90		120	
			cc.		cc.		cc.		cc.		cc.	
			% O ₂	O ₂	% O ₂	O ₂	% O ₂	O ₂	% O ₂	O ₂	% O ₂	O ₂
Phenol	10 cm.	53.56	20.75	6.97	20.38	6.84	20.38	6.84	20.38	6.84	20.38	6.84
Sucrose	10 cm.	52.74	20.75	7.14	19.31	6.64	18.00	6.19	16.75	5.76	15.38	5.29
Phenol	50 cm.	44.70	20.75	8.81	20.38	8.65	20.38	8.65	20.38	8.65	20.38	8.65
Sucrose	50 cm.	45.99	20.75	8.53	20.44	8.41	19.50	8.02	18.65	7.64	17.50	7.20
Phenol	100 cm.	42.45	21.00	9.38	20.63	9.22	20.63	9.22	20.63	9.22	20.63	9.22
Sucrose	100 cm.	42.80	21.00	9.31	20.19	8.94	19.44	8.62	18.69	8.29	17.69	7.84
Phenol	300 cm.	38.78	21.00	10.16	20.88	10.10	20.88	10.10	20.88	10.10	20.88	10.10
Sucrose	300 cm.	38.96	21.00	10.12	20.38	9.82	20.00	9.64	19.50	9.40	19.00	9.15
Phenol	1 Atm.	36.36	20.75	10.54	20.75	10.54	20.75	10.54	20.75	10.54	20.75	10.54
Sucrose	1 Atm.	36.18	20.75	10.57	20.25	10.32	19.69	10.03	19.19	9.78	18.88	9.62

Table 13. Aeration porosity, in percent, for the laboratory prepared cores of Webster silty clay loam at various tensions of water

Treatment	Tension (cm. of water)				
	10	50	100	300	1 Atm.
1% sucrose	10.8	22.2	27.6	34.1	38.8
15% phenol	9.4	24.4	28.2	34.4	38.5

slightly greater air filled pore space for diffusion than did the sucrose treated cores at the same tensions.

Discussions and Conclusions

It is remembered, in discussing the soil core experimental data and drawing conclusions from these data, that the cores were of constant length and constant bulk density and were prepared in the laboratory. Some of the cores were treated with 15% phenol solution to prevent microbial consumption of oxygen and others were treated with 1% sucrose solution to stimulate microbial consumption of oxygen. The effect of the treatment solution on microbial consumption was tested and it was found that 15% phenol solution was effective in preventing microbial consumption. Oxygen was consumed by the microorganisms in the cores treated with the

sucrose solution.

In the experimental apparatus for study of diffusion, it is worthy of mentioning that a true steady state was not attained. Since the partial pressure of oxygen continues to increase during the time interval of diffusion, only an approximate steady state was obtained. The lack of attaining a true steady state probably accounts in part for the fact that the diffusion lines of the plot of $\log P_o/(P_o - P)$ vs t (Figures 11-15) did not go through the origin when there was no consumption. Failure to include the coefficient b of equation (19) in the plotting accounts for part of the failure when there is consumption.

From the oxygen diffusion data in Table 10 on soil cores, it is evident that no measurable quantity of oxygen diffused through the soil cores at 10 cm. of water tension. The cores did, however, have about 10% aeration porosity. Blocked pores probably accounts for the lack of diffusing of oxygen through the cores. The blocked pores contribute to the porosity but not to diffusion. The quantity of oxygen diffusing through the soil cores in Table 10 increased as the water tension increased. This is due to increasing the volume of air filled pores as the water tension becomes greater. The quantity of oxygen diffusing through the sucrose treated cores was smaller than that through the phenol treated cores. This effect was more pronounced at the lower

tensions. The decreased quantity of oxygen that diffused through the sucrose treated cores is a result of the consumption of oxygen by the soil microorganisms.

The diffusion data was applied to equation (23) of the theoretical considerations section. In this equation it is assumed that the consumption is negligible. This is the equation that is usually applied to diffusion data and it is assumed that consumption is negligible during the time of the determination. From the diffusion data in Table 10 and Figures 11-15, it is evident that the apparent diffusion coefficient (slope of line of plot $\log P_0/(P_0 - P)$ vs t) is not the same for the phenol treated cores as for the sucrose treated cores. This difference in slope can be explained in part by the slightly greater porosity in the phenol treated cores. However it is also a result of increased consumption of oxygen by the soil microorganisms. If one neglects the consumption of oxygen by the soil microorganisms in the determination of the apparent diffusion coefficient of oxygen in the soil, serious error can be obtained at low water tensions. At low water tensions it would be desirable to develop a method of controlling oxygen consumption in the determination of the apparent diffusion coefficient. At high tensions of water, the amount of oxygen consumed may be neglected. The amount of oxygen diffusing at these high water tensions is apparently large compared to the amount of oxygen consumed

within the core.

The plots of D/D_0 vs porosity for the soil cores gave a good linear relationship. This plot had a zero D/D_0 intercept at about 17% porosity. This suggests that some of the pore space was in the form of blocked pores. These blocked pores contributed to the porosity but not to diffusion.

In field soil, one is concerned with both diffusion and consumption of oxygen in determining the concentration of oxygen at a particular depth and time. The laboratory core diffusion data seems to be in agreement with the field oxygen concentration data obtained during 1953. It will be recalled that in the surface 3 inches of soil, the oxygen concentration was maintained at a high level throughout most of the growing season. Since the moisture content was low, in this zone, it is to be expected that consumption of oxygen would be negligible. In general, the oxygen concentration during 1953 decreased with increasing depth to the 2-foot zone. Thus the diffusion impedance must have increased in these soils and the overall length at which consumption took place increased. These two effects probably resulted in a decreased oxygen concentration with increasing depth to the 2-foot zone. Because of the high moisture content in the 3-foot zone, the diffusion impedance would be great. The consumption of oxygen by the soil microorganisms would, however, be small in this zone as a result of low organic matter content. Even though

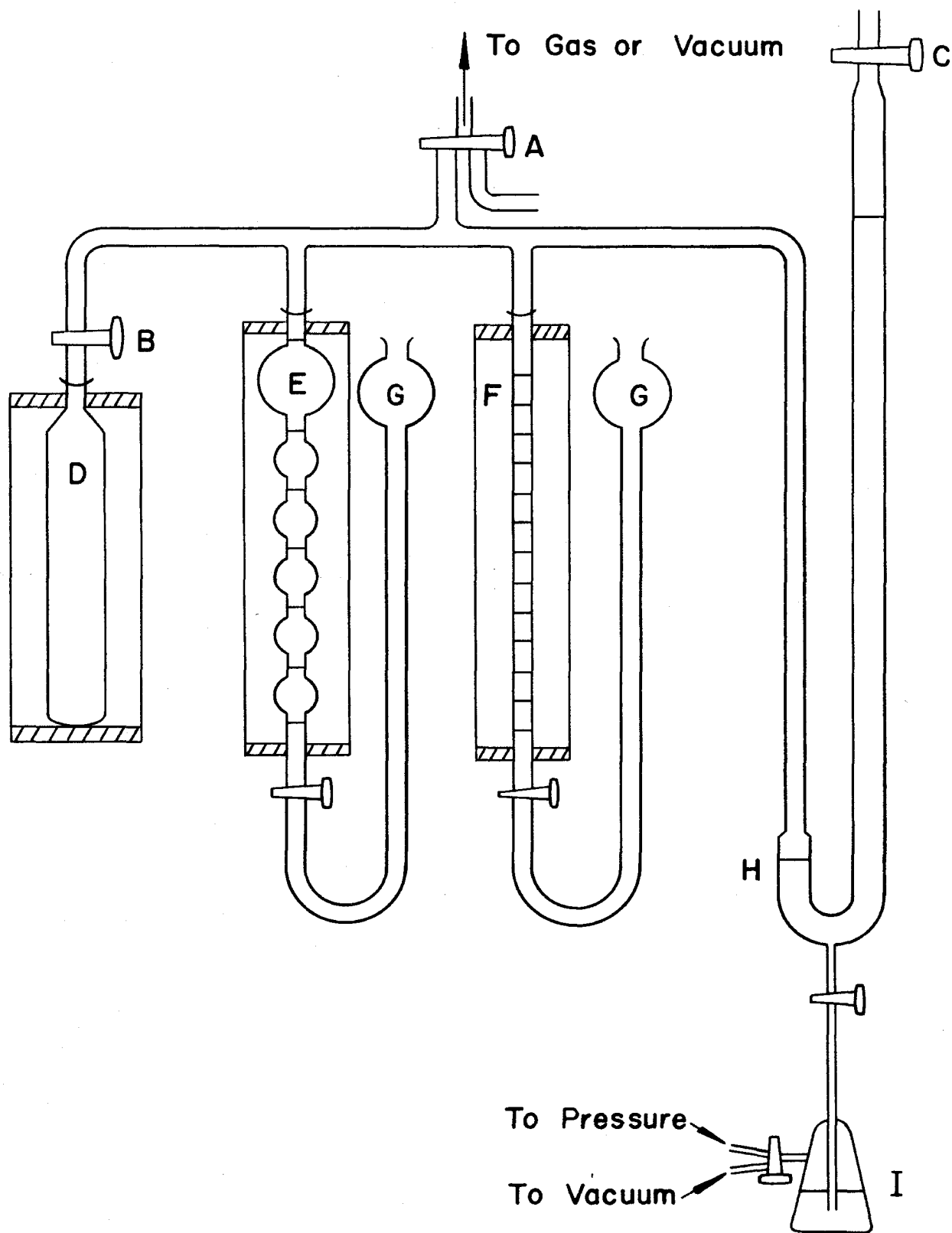
the diffusion impedance would be small in this 3-foot zone, the lack of consumption would result in a high oxygen concentration. The effect of oxygen consumption by soil microorganisms is most pronounced in the field oxygen concentration data during 1953 in the 2- and 3-foot zones where isolated soil gas concentrations were at a low level for long periods of time. Because of the high moisture content in these zones, blocking of the soil pores was more probable. Oxygen consumption by the soil microorganisms within this blocked volume resulted in an unusually low oxygen concentration.

SORPTION OF OXYGEN BY UNSATURATED SOILS AND VERMICULITE

Methods

A diagram of the apparatus used to measure the sorption of oxygen is shown in Figure 17. In this investigation, sorption refers to the total uptake of gas and therefore includes both absorption and adsorption. The sorbing materials used in the apparatus were, for one set of experiments, oven-dry and air-dry soil and sand; and, for another set of experiments, vermiculite and an Edina subsoil moistened to different moisture percentages. The sorbing apparatus consisted of a pyrex glass tubing assembly and flasks. All the connecting tubing was made from 2 3/4 mm. capillary tubing. The adsorption flask D which was constructed to contain the vermiculite or other adsorbants, was connected to the assembly with a No. 28 ground glass ball joint connection. A volume-measuring flask E was constructed with a large volume at the top and five small volumes connected in series to the bottom of the large volume. Capillary tubing was used to connect all of the volumes. Two volume-measuring flasks such as the one E shown in Figure 17 were constructed. One contained a large volume of approximately 200 cc. and five small 20 cc. volumes and the others contained a large volume of 300 cc. and five small 20 cc. volumes. These flasks were sufficient

Figure 17. A diagram of the sorption measuring apparatus showing essential parts



in number and size to measure, in conjunction with a burette F the large range in dead space (space not occupied by the adsorber) in adsorption flask D. The extent of the dead space in flask D must be determined to determine in turn the volume of oxygen needed to occupy this dead space. Helium gas is introduced into the dead space to determine the dead space volume. The volume of helium occupied by the dead space is subtracted from the volume of oxygen subsequently to be let into flask D. The difference in volumes yields the volume of oxygen adsorbed.

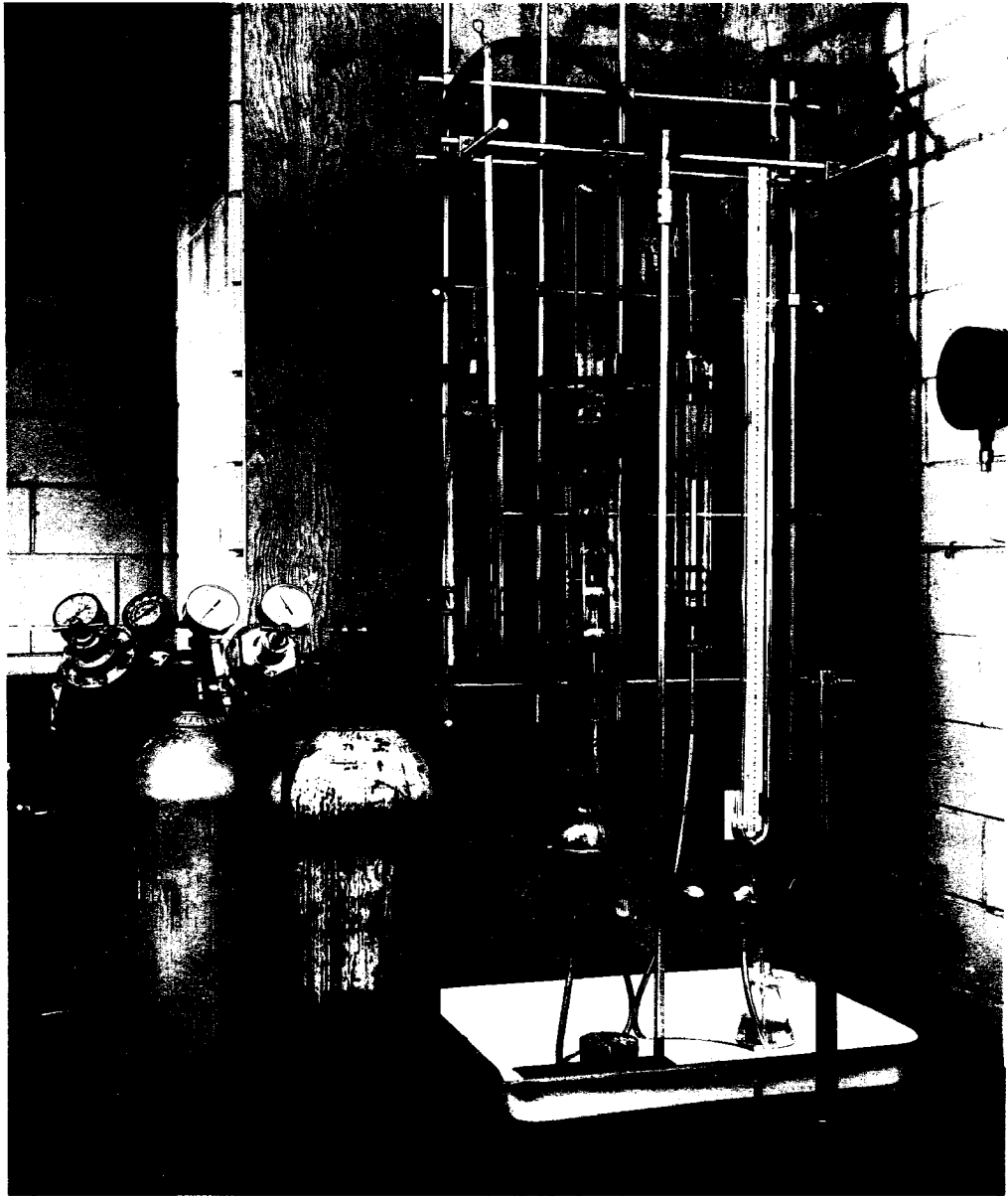
Each large and small volume of the measuring flask E was accurately calibrated with water at 25° C. The measuring flask E was connected to the assembly with a No. 12 ground glass ball joint connection. The burette F for the fine volume measurements, was constructed from a 10 ml. burette which had 0.05 ml. divisions. This burette was accurately calibrated with mercury at 25° C. The burette was connected to the assembly with a No. 12 ground glass ball joint connection. Leveling bulbs G, containing mercury not indicated in the figure, were used to decrease or increase the volume of the measuring volume E and of the volume in the burette F. A mercury manometer was connected to the assembly at H to measure the pressure inside the assembly. The manometer was evacuated through stopcock C. Pressure or vacuum was used in flask I to adjust the height of mercury at H. A cathetometer

was used to measure the level of the mercury. All of the stopcocks in the assembly were vacuum stopcocks. High vacuum grease was used in all stopcocks and ball joint connections. Water jackets were constructed around flasks D, E, and F. These were made of plexiglas tubing. Water from a constant temperature bath was constantly circulated through the water jackets. The water bath was maintained at a temperature of $25^{\circ}\text{C.} \pm 0.1^{\circ}\text{C.}$

The assembly was evacuated with a Welch duo-seal pump. A vapor trap of dry-ice in alcohol was placed in front of the pump. Stopcock A served as an opening for evacuating the assembly or introducing gas as desired. Gas cylinders were used as a source of helium and oxygen. Oxygen is the gas, the adsorption of which is desired to be known, helium is used to determine the dead space. The helium gas was obtained from the Mathison Chemical Company and the oxygen obtained from Balbach Company. The same gas cylinders were used throughout the experiment. The gas was introduced into the assembly through stopcock A. The gas first passed through 50 feet of 1/8-inch copper tubing which was placed in the constant temperature bath. The barometric pressure was recorded from a wall-type barometer.

The sorption apparatus was assembled in a constant temperature room as shown in Figure 18. The temperature of the room was set at $25^{\circ}\text{C.} \pm 1.5^{\circ}\text{C.}$ Because of excessive

Figure 18. A photograph of the sorption apparatus in the constant temperature room



weight caused by the large quantity of mercury used in measuring glass E, the flask E and leveling bulb G were supported with plaster of paris molds.

The soil samples used in the experiment were collected in the field, air-dried, and passed through an 8 mm. sieve. For the set of experiments in which air-dry materials were used the soil materials were a Webster silty clay loam, an Ida silt loam and an Edina silt loam, each sample being taken from the zero to 6-inch depth. In the second set of experiments (with moistened materials), a subsoil in the Edina silt loam at 23 inches depth was used. The Webster and Edina soils have been described. The Ida soil is a loess. The sand used was quartz sand obtained locally. The vermiculite used was exfoliated vermiculite and is sold under the trade name "Terra-Lite". The air-dry samples of soil and sand were placed in a container in the constant temperature bath one week before oxygen adsorption was determined.

It is necessary, in correcting for helium solubility, and for theoretical solution of oxygen in the adsorbed water, to know the vapor pressure of the moisture adsorbed on the moist vermiculite and Edina subsoil. The vapor pressure on the air-dry samples were neglected. The vapor pressure of the water on the vermiculite and Edina subsoil was determined by evacuating the material in a closed system connected to the manometer and a vacuum pump. In a first evacuation of

the system, adsorbed and dissolved air was removed (with some water vapor molecules). The system was then frozen, at dry ice-alcohol temperature, and reevacuated to remove any remaining gas or ice vapor molecules. The vapor pressure produced when the material was subsequently thawed to 25° C. was taken as the vapor pressure of the water on the vermiculite and Edina subsoil. This procedure was repeated two or three times before a constant vapor pressure was obtained. A sensitive cathetometer was used to measure the level of mercury in the manometer. The cathetometer has a sensitivity of 0.1 mm.

Procedure for Measuring Oxygen Sorption

On dry materials the line to the vacuum pump was connected to stopcock A of Figure 17 and stopcock A was opened and the system evacuated. To evacuate adsorption flask D, stopcock B was opened periodically during the evacuation. After evacuation, stopcocks A and B were closed and the connection to the vacuum pump removed. The helium tank was then connected to stopcock A and stopcock A was turned so helium would flow through stopcock A into the atmosphere. This procedure removed all other gases from the connecting lines to stopcock A. Stopcock A was next turned so that helium flowed into the adsorption apparatus until slightly greater than atmospheric pressure was reached. The connection from

the helium source to stopcock A was removed and stopcock A turned to allow helium to escape to the atmosphere until the helium pressure in the adsorption apparatus was at atmospheric pressure. Stopcock A was closed off from the atmosphere. The cathetometer was set on the mercury meniscus in the manometer. The barometric pressure was recorded. Stopcock B was opened to the evacuated sorption chamber D and the mercury level in the measuring volume E was raised to about the volume of the dead space in adsorption flask D. The raising of the mercury offset approximately the pressure loss in the system caused by the entry of helium into D. The raising of the mercury level in E so that the dead space would be sufficiently well approximated required two or three tries. The mercury level in the burette F was raised to complete the bringing of the pressure inside the adsorption apparatus back to atmospheric pressure as indicated by the cathetometer. The volume required to reduce the space inside the adsorption apparatus to the point where the pressure in the system was brought back to atmospheric after stopcock B was opened was recorded as the dead space. Because of the water vapor in adsorption flask D, stopcock B was not opened continuously during the adjustment of valves. It was only opened at brief intervals during the volume adjustments.

The adsorption assembly was reevacuated and the same procedure as above was repeated except that oxygen was

introduced instead of helium. Sorption equilibrium with oxygen was reached on the dry material in less than 30 minutes. Equilibrium was considered reached when the mercury level in burette F did not have to be further raised to maintain the system at atmospheric pressure. The difference in the volume of oxygen and the volume of helium was considered to be the volume of sorption by the material in the adsorption flask D. The above procedure has the advantage over other methods which might have been used for measuring the dead space, in that the dead space as determined by helium and the space of the oxygen are measured in a similar way (both volumetrically).

On the wet vermiculite and Edina subsoil, the same basic procedure was followed as on the dry materials. But, during the evacuation, stopcock B was opened for a period of three to four seconds at intervals of five minutes to remove the sorbed gases in adsorption flask D without removing large quantities of water vapor. The stopcock B was opened seven times by this procedure during the evacuation process. This intermittent procedure of removing the sorbed gases from the adsorption flask D has the advantage that large quantities of water vapor are not removed. Thus the dead space can be determined at the same moisture level which will exist when the oxygen sorption is determined. The helium dead space was corrected for the helium dissolved in the adsorbed water

to give the true dead space in the adsorption flask. The helium was assumed to be dissolved to the same extent in the adsorbed water as in pure water and therefore the Bunsen adsorption coefficient of 0.00860 was used to determine the quantity of helium dissolved, the value 0.00860 being used at each moisture content. The vermiculite and Edina subsoil were wetted with distilled water and the different moisture levels subsequently obtained by vacuum drying. During the vacuum drying, it was found that the temperature of the adsorption flask was lowered. The adsorption flask was therefore allowed to come to 25° C. before the next adsorption measurement was made. The sorption of oxygen on vermiculite and Edina subsoil were determined at a number of different moisture contents from wetness to dryness. By knowing the weight of the flask and the oven-dry weight of adsorber the moisture content could be determined at the different intervals of dryness. The reaching of the sorption equilibrium for oxygen on the wet material required about 1 1/2 hours. The volume of oxygen sorbed was converted to the volume of oxygen at 0° C. and 760 mm. pressure.

Because of the possibility of microbial consumption on the moist Edina subsoil, the moist soil in adsorption flask D was maintained in an atmosphere of helium at all times except in the brief time that sorption was determined.

Results

The results obtained in the oxygen sorption studies with dry sand and soil are shown in Table 14. The name of the sorbing material and the actual oven-dry weight of material used in these experiments is given in columns 1 and 2. This oven-dry weight and the amount of water present in the air-dry samples shown in column 3 were based on oven drying the material for 48 hours at 105° C. The volume of oxygen at standard temperature and pressure that was sorbed by each of the materials at 25° C. is given in column 4. Each of these values are the mean of three individual determinations on the same sorbing sample. The three determinations did not differ from each other by more than 10%. Then, for comparative purposes, the amount of oxygen that would dissolve in the water of the air-dry samples if it were free water was calculated and shown in column 5. In this calculation a value of 3.33×10^7 was used for Henry's constant (the k in $P = kX$; see page 16) and the vapor pressure of the water in the material was neglected since the materials were air-dry. Therefore, since the total pressure of the system during the oxygen sorption was always near 730 mm. of mercury, the values in column 3 were multiplied by the factor $(730 \times 32 \times 1000 / 1.429) / (18.016 \times 3.33 \times 10^7)$ which is equal to 0.0272 cc. of O_2 per gram of water. Here, aside from numbers mentioned,

Table 14. The sorption of oxygen at 25° C. on air-dry and oven-dry soil and sand

Soil ^a	Oven-dry wt. of soil	Wt. of water in soil	cc. of O ₂ sorbed by soil & water S.T.P. ^b	cc. of O ₂ soluble in the no. of gms. in column 3 if the water is free ^c	Ratio, columns 4 & 5 ^d	cc. of O ₂ sorbed per gm. of water & material
Sand air-dry	657.0	2.0	0.00	0.054	0.00	0.00000
Sand oven-dry	655.0	0.0	0.06	0.000	--	0.00009
Webster air-dry	340.1	15.4	2.17	0.419	5.18	0.00610
Webster oven-dry	297.7	0.0	23.54	0.000	--	0.07907
Ida air-dry	362.0	9.0	1.39	0.245	5.67	0.00375
Ida oven-dry	290.4	0.0	13.93	0.000	--	0.04796
Edina air-dry	346.0	9.5	1.69	0.258	6.55	0.00475
Edina oven-dry	286.4	0.0	15.93	0.000	--	0.05562
Edina subsoil air-dry	423.5	27.5	5.83	0.748	7.79	0.01293
Edina subsoil oven-dry	388.1	0.0	46.00	0.000	--	0.11852

^aThe soils are ungraded quartz sand, Webster silty clay loam, 0-6 inches; Ida silt loam, 0-6 inches; Edina silt loam, 0-6 inches; and Edina subsoil, 20-23 inches.

^bEach value represents the mean of three determinations.

^cValue of column 3 multiplied by 0.0272; see text.

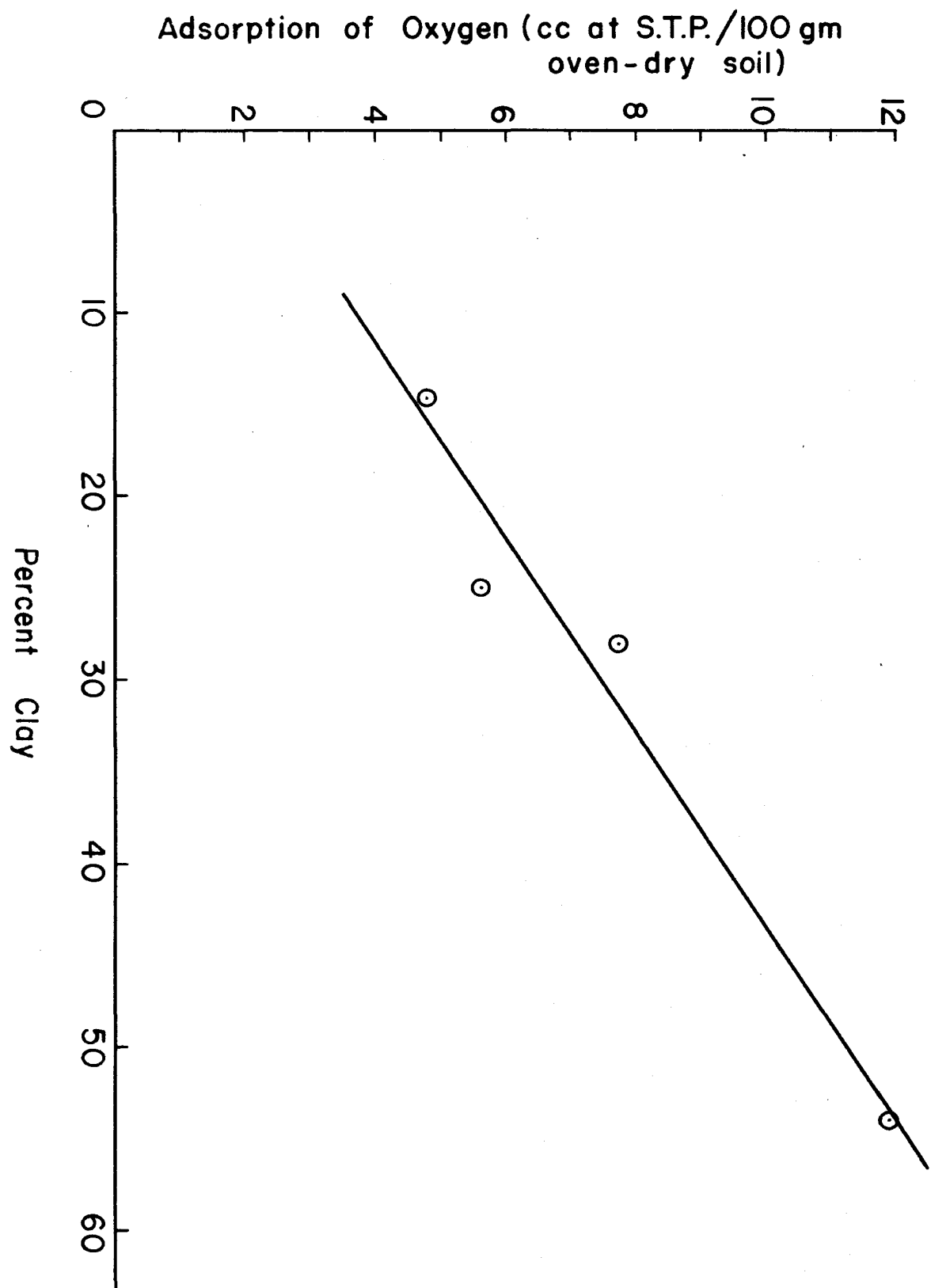
^dValue in column 4 divided by corresponding value in column 5, oven-dry soil excluded.

32 is the molecular weight of oxygen, 18.016 is the molecular weight of water (the number of moles of O_2 in the water are neglected in comparing the mole fraction of water plus oxygen), and 1.429 is the density of oxygen in grams per liter at S.T.P. Column 6 gives the ratio of oxygen adsorbed by free water to oxygen adsorbed by the same amount of water on the soil. The last column gives the sorption of oxygen in cc. per gram of soil plus water. The figures are all not significant.

The clay content of the soil samples was determined and found to be 54.0, 25.0, 28.0, and 14.7% for the Edina subsoil, Edina silt loam, Webster silty clay loam, and Ida silt loam, respectively. The relationship between this clay content and the oxygen sorbed is shown in Figure 19 where the oxygen sorbed by the oven-dry soils is plotted as a function of the clay content. The curve in the figure is a regression line calculated from the data.

In the oxygen sorption studies with the wet sorbing materials the vapor pressure of the water on the material contributed to the total pressure in the system. A determination of this vapor pressure was therefore made so a correction could be made in the calculation of the effect of helium solubility on the dead space and in the calculation of the theoretical solubility of oxygen in the water of the system if it were free water. In the case of the vermiculite the vapor pressure of the unsaturated vermiculite was deter-

Figure 19. The relationship between the oxygen sorbed by oven-dry soils at 25° C. and the clay content of these soils

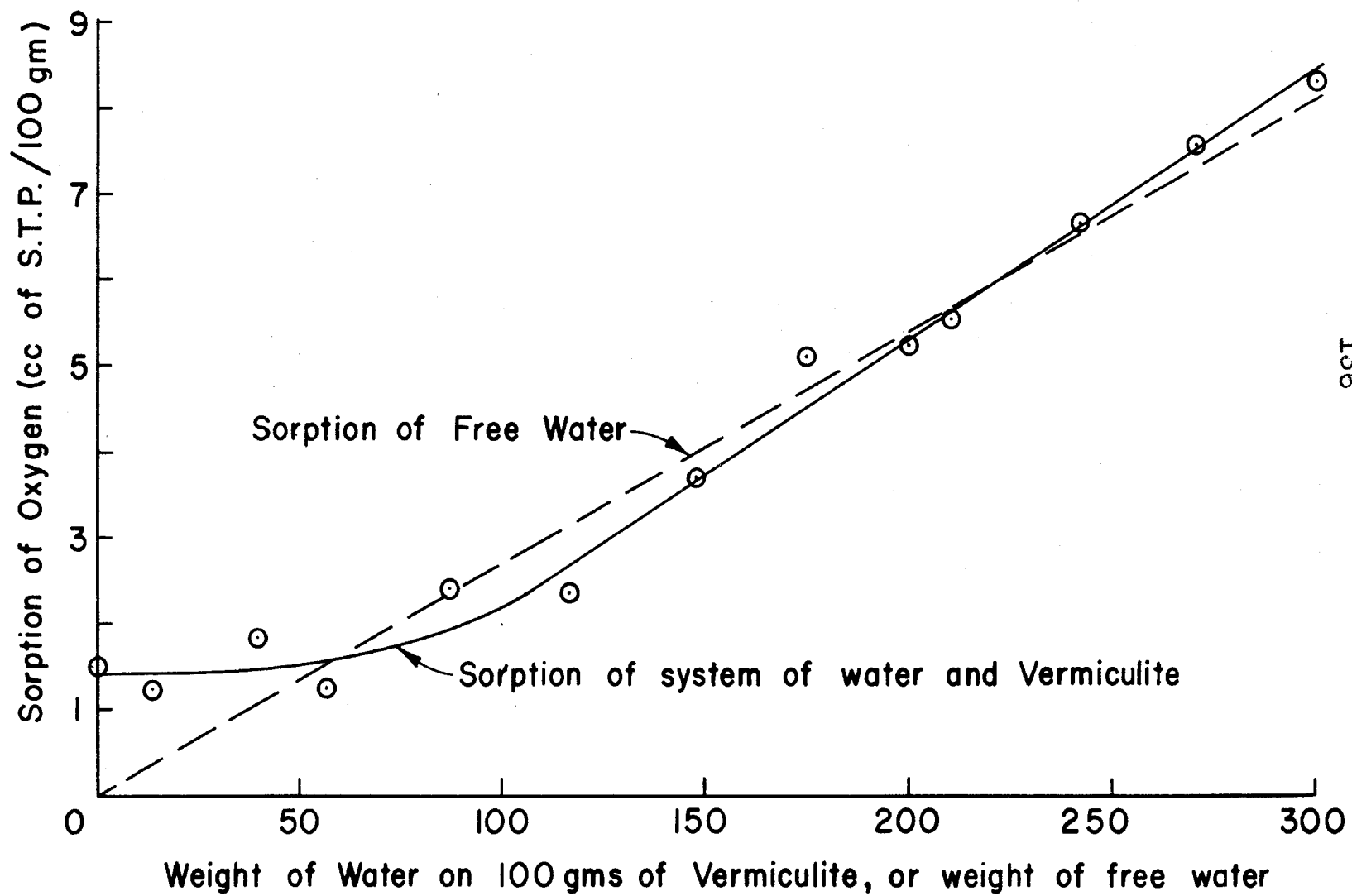


mined between 80% and 204% water. A constant vapor pressure of 22.8 mm. at 25° C. was obtained within this range. In order to compare this value with that of pure water, the vapor pressure of redistilled water was also determined by the same procedure. A vapor pressure of 22.8 mm. at 25° C. was obtained.

The accuracy of the method used to determine the sorption of oxygen depends largely on the accuracy of the dead space determination. The dead space determined with helium in the experiments with wet vermiculite was therefore plotted as a function of the moisture content of the vermiculite and a regression calculated. The slope of the regression line was 0.976. When this value is corrected for the vapor pressure of water, 22.8 mm., there results a slope of 1.007 for the true dead space as a function of the moisture content of the unsaturated vermiculite. To make this correction the average pressure over which the experiment was conducted, that is 738.3, was divided into 22.8 and the quotient 0.031 added to 0.976 gives the slope of the true dead space as a function of moisture content of the unsaturated vermiculite. Since the slope of the corrected dead space as a function of the moisture content is very nearly one, it is assumed that the method is an accurate method of determining sorption.

The results of the oxygen sorption as a function of the moisture content of the vermiculite are shown in Figure 20.

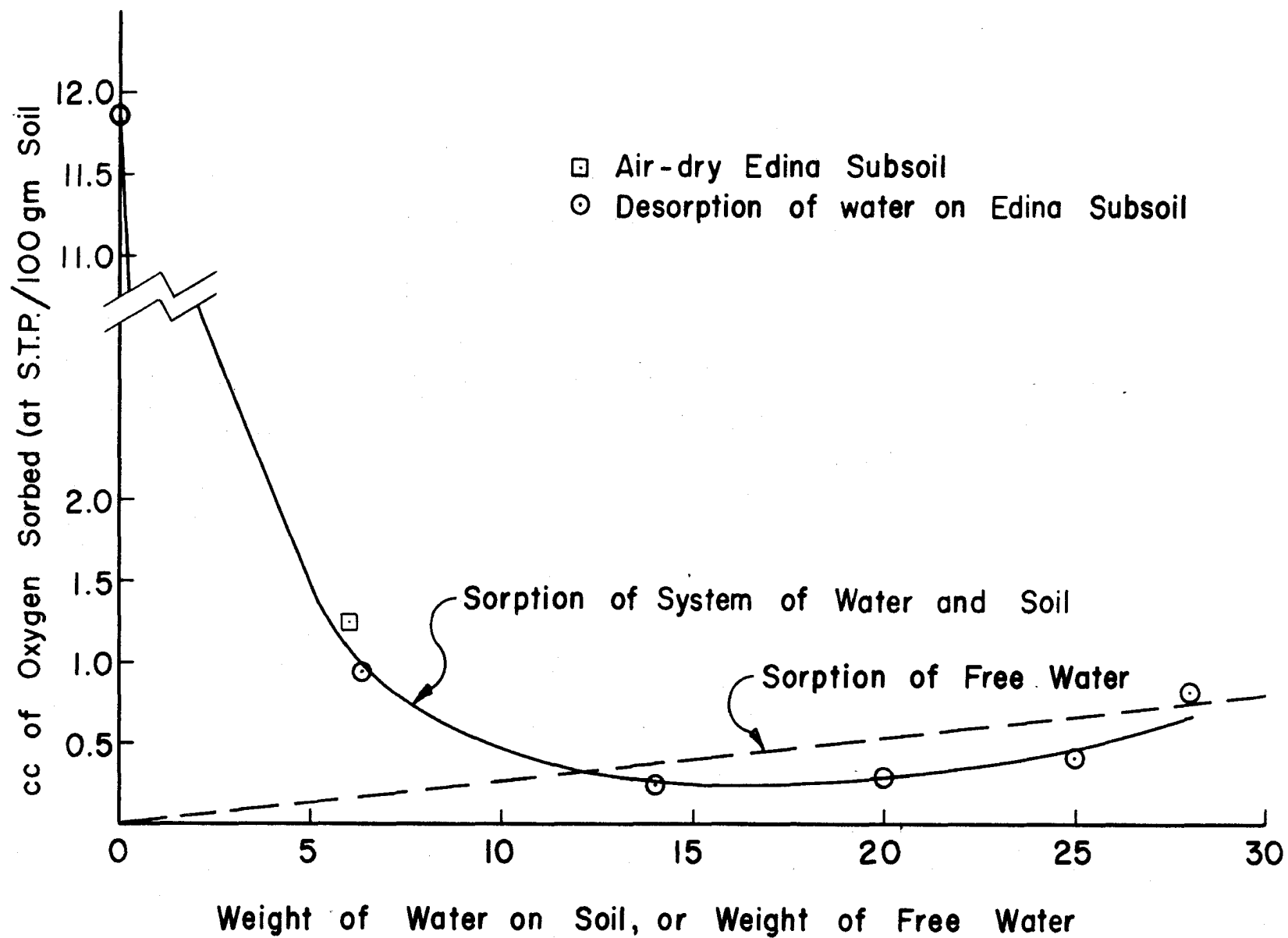
Figure 20. The sorption of oxygen at 0° C. and 760 mm. by exfoliated natural vermiculite as a function of the moisture content of the vermiculite; the solubility of oxygen in equivalent amounts of free water is shown by the dashed line (data points apply to the solid line)



The sorption in cc. at standard temperature and pressure per 100 grams of material is plotted as a function of the moisture on the 100 gram sample. The moisture values given in this figure are based on the weight of vermiculite when oven-dried for 24 hours at 105° C. The dashed line is the solubility of oxygen in pure water calculated with a value of 3.33×10^7 for Henry's law constant and a partial pressure of oxygen of 715.5 mm. This value for the partial pressure of oxygen was obtained by subtracting the vapor pressure of water from the average total pressure of the system over which the experiment was conducted. The slope of this line is 0.0267. The sorption of oxygen by the wet vermiculite appeared to be a linear relationship for the moisture range 100 to 300 grams of water. Therefore a regression line was calculated for this range of moisture. The slope of the regression line was found to be 0.0315. A line which best fit the data was drawn for the remainder of the curve.

The results of the sorption of oxygen by the moist Edina subsoil are shown in Figure 21. The sorption in cc. at standard temperature and pressure were plotted as a function of the grams of water on the 100 grams of soil. The dashed line is the solubility of oxygen in the equivalent amount of pure water assuming a Henry's law constant of 3.33×10^7 . In this system the average total pressure used in these experiments was 743.0 and the vapor pressure of water was

Figure 21. The sorption of oxygen at 0° C. and 760 mm. pressure by moist Edina subsoil as a function of the moisture content of the soil; the solubility of oxygen in equivalent amounts of free water is shown by the dashed line (data points apply to the solid line; weight of water on soil is for 100 grams oven dry)



found to be 20.0 mm. at 28.6% moisture, 19.1 mm. at 25.1% moisture, 18.4 mm. at 19.9% moisture, 17.5 mm. at 14.2% moisture, and 6.0 mm. at 6.3% moisture. This gives an average vapor pressure of water of 16.2 over the range of moisture contents. Thus a partial pressure of oxygen of 726.8 mm. of mercury was used in the calculation of theoretical oxygen solubility curve. The moisture values are again based on the oven dry weight of soil.

Discussions and Conclusions

The oxygen sorbed by air-dry or oven-dry sand was found to be negligible. This is to be expected since the surface area of the coarse material used was very small and the amount of water in the air-dry system available for dissolving oxygen was small. It is suggested from these results that oven-dry quartz sand be used periodically in future studies as a check on the apparatus and the skill of the operator.

An appreciable quantity of oxygen was sorbed by the oven-dry soils. The amount adsorbed is comparable to that observed by Makower et al. (33) with Cecil soil. The adsorption of oxygen by the oven-dry soils was, however, not constant per unit mass of soil for the different soils as may be seen in the last column of Table 14. On the other hand, a good relationship was found between the amount of oxygen

adsorbed and the clay content of the soils as shown in Figure 19. This observation is consistent with the conclusions of others (33, 39) that gas adsorption in soils is primarily determined by the clay content.

The adsorption of oxygen by the air-dry soils, as is seen by comparing values in column 4 of Table 14, is considerably less than that of oven-dry soils. The adsorption is, however, considerably greater than could be accounted for by ordinary solubility of oxygen in the water in the sample. It is apparent from the values in column 6 of the table that the soil water systems sorbed five to eight times as much oxygen as the water in the system alone could dissolve if it behaved as free pure water. It is therefore apparent that the major portion of the oxygen sorbed by air-dry soil is adsorbed by the soil particles even though there is some water present. The decrease in sorption observed on one gas from the oven-dry to air-dry soils indicates, however, that the addition of water does interfere with the adsorption of gases by the soil. These results are in good agreement with those of Brooks (9) for the montmorillinite and illite type of clay mineral. The soils investigated in the present experiment are probably of the montmorillonite-illite type of clay mineral. Surface area measurements were not made on these soils, therefore it is not possible to calculate if there is enough water in the air-dry soil to give a

monomolecular layer on the surfaces. Thus it is also impossible to conclude at this point whether gas sorption is occurring in spite of the presence of enough water to form a close packed monomolecular layer. In such a consideration it should also be noted that Brooks (9) questions the validity of speaking of a monomolecular layer of polar molecules like water on clay mineral surfaces. Then if the first layer of water is an open hexagonal arrangement of water molecules it does seem possible that sites for gas adsorption may still exist even in the presence of water.

Sorption was studied on vermiculite and Edina subsoil moistened to different moisture contents. Vermiculite was selected because it has an expanding type of lattice and also because it will hold large quantities of water and still remain very porous for gas measurement. Edina subsoil was selected because it gave the largest amount of oxygen adsorbed. The sorption of oxygen by the vermiculite-water system was determined as the wet vermiculite sample was progressively dried because the apparatus was more adaptable to this procedure. It should be noted that the large accordion-like flakes of exfoliated vermiculite were largely disintegrated by the successive evacuations and drying of the sample. At the end of the dehydration cycle the vermiculite was in a finely divided state.

From Figure 19, it is apparent that the oxygen sorption

by vermiculite did not increase when the material was oven-dried at 105° C. as did the soils. This observation does not support the statement by Gregg (23) that the surface area of vermiculite measured by nitrogen adsorption increases as the vermiculite is heated to remove water. Gregg did not indicate at what temperature this occurred. It is known from dehydration studies (25) that vermiculite will continue to lose water up to 550° C. without losing its ability to rehydrate. When saturated with divalent cations like Ca and Mg, which the natural vermiculite generally has on its exchange complex, the differential thermal analysis curves show endothermic peaks at 125° C. and 280° C. due to the loss of water. Now in the present oxygen sorption experiment the vermiculite was only dried to 105° C. It is therefore still quite possible that an increase in oxygen sorption may occur if more water is removed by higher drying temperatures. Since the silicate structure of vermiculite and montmorillonite are considered to be essentially the same it is to be expected that neither oxygen nor nitrogen will be adsorbed on intracrystalline surfaces; but at this point there is no reason to believe that the effect of water on gas adsorption on the external surfaces should be different in the two clays.

It is extremely interesting to note that over the moisture range from 0 (105° oven-dry) to 75% the sorption of oxygen is relatively constant. Since the published data (9)

for gas sorption on other clays do not extend beyond the moisture content of the air-dry state no comparison can be made with the other clays in this region. In view of the scatter of the points in the early part of the moisture range (Figure 20) further conclusions on the observation should await further verification of the points so far observed.

Over the moisture range of 75% to 300% moisture there was a linear relationship between the oxygen sorbed and the moisture content. Considering the experimental error the sorption curve is very nearly the same as the theoretical oxygen solubility curve. The slopes of the two lines were 0.0267 and 0.0315. With the limited data at hand there was no significant difference between the curves. Thus for all practical purposes one can conclude that the amount of oxygen taken up by wet vermiculite in this moisture range is equivalent to that dissolved in the adsorbed water.

It should be emphasized that the effect of moisture on the oxygen sorption by vermiculite was determined on a system that was progressively dehydrated. A similar study in which the vermiculite is progressively rehydrated should also be made.

The effect of higher moisture contents on the sorption of oxygen by soils was determined on the Edina subsoil because it had a very high clay content and thus a greater ability to

adsorb oxygen. As seen in Figure 21, the oxygen sorbed by the Edina subsoil was in excess of that which could be dissolved in the soil water when the moisture content was below 12%. At moisture contents between 14% and 25% there appeared to be a reduction in the amount of oxygen sorbed when compared to free water. When the moisture content was about 28%, the amount of oxygen sorbed was equivalent to that in free water.

From the data on the sorption of oxygen on the moist vermiculite and Edina subsoil, it appears that at moisture contents normally involved in field soils the amount of oxygen sorbed is only that which is dissolved in the soil water. This appears to be only a solubility process and the amount of oxygen adsorbed in the dry state is important at very low moisture contents. The solubility of oxygen in the soil water would however vary from one soil to the other depending upon the salt content. The decreased solubility of oxygen by the salts may be important in saline and alkaline soils.

GENERAL SUMMARY

The effect of improving the stability of the surface 6 inches of Webster silty clay loam and Edina silt loam on the depth distribution of oxygen in the gas phase as well as on other factors such as moisture content of the soil, potassium content of corn leaves and corn yields was investigated on both soils during the 1953 growing season. A synthetic organic material was used to improve the aggregate stability of the soil. After application of this material, a remarkable improvement in the water stability of the treated aggregates was observed on both soils. The improved aggregate stability had no measurable effect on the oxygen concentration of either soil. The oxygen concentrations were low at the beginning of the growing season when the moisture content of the soil was high and the concentrations increased toward the end of the growing season when the moisture content of the soil decreased. In general, the oxygen concentration decreased with increasing depth on both soils to the 2-foot zone in the early portion of the growing season. However the oxygen concentrations at the 3-foot zone were higher than those at the 2-foot zone. The heterogeneity of the soil oxygen concentration became greater with increasing depth in the soil profile.

The moisture content of the surface soil of Edina silt

loam treated with the synthetic organic material was higher than the untreated soil in the early spring of 1953. However, by July 17 the reverse condition was found. This reversal in moisture content of the soil is a result of the rough surface caused by stabilizing the aggregates. The rough stabilized surface gives a greater evaporating surface. In the early spring when the soil temperature is low, evaporation is negligible; however, later in the summer when the soil temperature becomes greater the rough surface of the treated soil gives greater evaporation.

The potassium content of the corn leaves tended to be higher on the Edina silt loam soil treated with the synthetic organic material. An increase in corn yields of about 10 bu./acre was obtained on the Edina silt loam as a result of applying the synthetic organic material to the surface 6 inches of soil. The general increase in corn yields was obtained on the Webster silty clay loam as a result of the application of the synthetic organic material; however, the highest yields were observed on this soil when treated with fertilizer plus the synthetic organic material.

The effect of consumption of oxygen by soil microorganisms on the total diffusion of oxygen and the diffusion constant of the soil was investigated using laboratory prepared soil cores of Webster silty clay loam. At low tensions of water (high moisture content), the consumption of oxygen

by the soil microorganisms reduced the total quantity of oxygen diffusing through the soil cores and likewise reduced the diffusion constant of the soil for oxygen. On the other hand, at high tensions of water (low moisture content) the consumption of oxygen by the soil microorganisms had little effect on the total quantity of oxygen diffusing through the soil cores. Diffusion in the laboratory prepared soil cores gives a more complete explanation of the soil oxygen concentration observed on Webster silty clay loam and Edina silt loam during the 1953 growing season. In the early spring, when the moisture content was high the diffusion impedance was also high and a low oxygen concentration was found at the 1- and 2-foot zones. The oxygen concentrations at the 3-foot zone, however, were found to be higher than at the 2-foot zone. Even though the diffusion impedance was also high in the 3-foot zone, the consumption of oxygen by the soil microorganisms was low as a result of low organic matter content; therefore, the oxygen concentration in this zone remained high. Toward the end of the growing season the diffusion impedance became low since the moisture content was low and the oxygen concentrations of the soil at all depths increased. The heterogeneity of oxygen concentrations in the soil with increasing depth was a result of blocking of the soil pores due to the high moisture content of the soil and consumption of oxygen within the blocked region.

The sorption of oxygen by oven-dry and air-dry Edina surface, Edina subsoil, Webster surface, Ida surface soils, and quartz sand as well as by vermiculite and Edina subsoil moistened to different moisture contents was investigated. The oven-dry soils sorbed more oxygen than the air-dry soils per unit mass of material. There was essentially no sorption of oxygen by sand. The sorption of oxygen by the air-dry soil was, however, greater than could be accounted for by the solubility of oxygen in the water in the soil. A good linear relationship was found between the clay content of the soil and the amount of oxygen adsorbed by the oven-dry soils. In the moisture range between 75% to 300%, the sorption of oxygen by unsaturated vermiculite appeared to be solubility of oxygen in the water alone. At moisture contents below 75%, the sorption of oxygen by the unsaturated vermiculite was greater than could be accounted for by solubility in the water alone. The sorption of oxygen in the unsaturated Edina subsoil at moisture contents below 12% was also greater than could be accounted for by solubility in the water. In the moisture range between 14% to 28% on the Edina subsoil, there appeared to be a reduction in the solubility of oxygen in the soil water as compared to free water. The solubility of oxygen in soil water may be important in soils of excessive salt concentrations such as saline and alkaline soils.

REFERENCES

1. Adams, N. L. The Physics and Chemistry of Surfaces. Oxford Univ. Press, London. 1930.
2. Akerlöf, G. The Solubility of Nobel Gases in Aqueous Salt Solutions at 25° C. J. Am. Chem. Soc. 57: 1196-1201. 1935.
3. Albright, P. L. and Williams, J. W. Electrical Forces Between Ions and Neutral Molecules in Aqueous Solutions, A Study of the "Salting-Out" Effect. Trans. Faraday Soc. 33:247-256. 1937.
4. Blake, G. R. and Page, J. B. Direct Measurement of Gaseous Diffusion in Soils. Soil Sci. Soc. Proc. 13:37-41. 1948.
5. Boynton, D. Seasonal Variations of Oxygen and Carbon Dioxide in Three Different Orchard Soils During 1938 and its Possible Significance. Proc. Am. Soc. Hort. Sci. 36:1-6. 1939.
6. Boynton, D. Soils in Relation to Fruit Growing. XV. Seasonal and Soil Influences on Oxygen and Carbon Dioxide Levels of New York Orchard Soils. N.Y. (Ithaca) Agr. Expt. Sta. Bul. 763. 1941.
7. Boynton, D. and Compton, O. C. Normal Seasonal Changes of Oxygen and Carbon Dioxide Percentages in Gas from the Larger Pores of Three Orchard Subsoils. Soil Sci. 57:107-117. 1944.
8. Boynton, D. and Reuther, W. A Way of Sampling Soil Gases in Dense Subsoil and Some of its Advantages and Limitations. Proc. Soil Sci. Soc. Am. 3:37-42. 1938.
9. Brooks, C. S. Nitrogen Adsorption Experiments on Several Clay Minerals. Soil Sci. 79:331-347. 1955.
10. Brunauer, S. The Adsorption of Gases and Vapors. Volume 1, Physical Adsorption. Princeton University Press, Princeton, N.J. 1945.
11. Brunauer, S. and Emmett, P. H. Adsorption Isotherms on Soil Colloids. J. Am. Chem. Soc. 59:26-82. 1937.

12. Buckingham, E. Contributions to Our Knowledge of the Aeration of Soils. U. S. Dept. Agr. Bur. of Soils Bul. 25. 1904.
13. Cady, H. P., Elsey, H. H. and Berger, E. V. The Solubility of Helium in Water. Jour. Am. Chem. Soc. 44:1456-1461. 1922.
14. Cornet, I. Sorption of NH_3 on Montmorillonite Clay. J. Chem. Phy. 11:217. 1943.
15. De Vries, D. A. Some Remarks on Gaseous Diffusion in Soils. Trans. 4th Int. Cong. Soil Sci. 2:41-43. 1950.
16. Emmett, P. H., Brunauer, S. and Love, K. S. The Measurement of Surface Area of Soils and Soil Colloids by the Use of Low Temperatures van der Waals Adsorption Isotherm. Soil Sci. 45:57-65.
17. Escard, J. Adsorption de l'Azote à Bosse Temperature Pore la Montmorillonite; Influence de l' Eau Residuelle et des Cations Exchangeables. Trans. 4th Intern. Cong. Soil Sci. 3:71. 1950.
18. Findlay, A. and Creighton, H. J. M. The Influence of Colloids and Fine Suspension on Solubility of Gases in Water. Part I. Solubility of Carbon Dioxide and Nitrous Oxide. J. Chem. Soc. (London) 97:536. 1910.
19. Findlay, A. and Creighton, H. J. M. The Influence of Colloids and Fine Suspensions on Solubility of Gases in Water. Part II. Solubility of Carbon Dioxide and Hydrogen. J. Chem. Soc. (London) 101:1459. 1912.
20. Fox, C. J. J. On the Coefficients of Absorption of Nitrogen and Oxygen in Distilled Water and Sea-Water, and of Atmospheric Carboric Acid in Sea-Water. Trans. Faraday Soc. 5:68-87. 1909.
21. Furr, J. R. and Aldrich, W. W. Oxygen and Carbon Dioxide Changes in the Soil Atmosphere of an Irrigated Date Garden on Calcareous Very Fine Sandy Loam Soil. Am. Soc. Hort. Sci. Proc. 42:46-52. 1943.

22. Glasstone, S. Textbook of Physical Chemistry. 2nd ed. E. Von Nostrand Company, Inc., New York. 1952.
23. Gregg, S. J. The Production of Active Solids by Thermal Decomposition. Part I. Introduction. J. Chem. Soc. (London) 3940-3944. 1953.
24. Gregg, S. J. and Stephens, M. J. The Production of Active Solids by Thermal Decomposition. Part III. The Calcination of Kaolinite. J. Chem. Soc. (London) 3951-3956. 1953.
25. Grim, R. E. Clay Mineralogy. McGraw-Hill Book Co., Inc., New York. 1953.
26. Hildebrand, J. H. and Scott, R. L. The Solubility of Non-electrolytes. 3rd ed. Reinhold Publishing Co., New York. 1950.
27. Hogan, R. Movement of Carbon Disulfide Vapor in Soils. Hilgardia 14:83-118. 1941.
28. International Critical Tables of Numerical Data, Physics, Chemistry, and Technology. Vol. 3. McGraw-Hill Book Co., Inc., New York. 1928.
29. Jamison, V. C. The Significance of Air Adsorption by Soil Colloids in Pycnometric Measurements. Soil Sci. Soc. Am. Proc. 17:17-19. 1953.
30. Keenan, A. G., Mooney, R. W. and Wood, L. A. The Relation Between Exchangeable Ions and Water Adsorption on Kaolinite. J. Phy. Chem. 55:1462-1474. 1951.
31. Lamb, A. B. and Woodhouse, J. C. Adsorption by Dehydrated Chabosite as a Function of the Water Content. J. Amer. Chem. Soc. 58:2637-2646. 1936.
32. Lannung, A. The Solubility of Helium, Neon, and Argon in Water and Some Organic Solvents. Jour. Amer. Chem. Soc. 52:68-80. 1930.
33. Makower, B., Shaw, T. M. and Alexander, L. T. The Specific Surface and Density of Some Soils and Their Colloids. Soil Sci. Soc. Amer. Proc. 2: 101-108. 1938.

34. Matheson, A. M. and Walker, G. F. Crystal Structure of Magnesium Vermiculite. *Am. Mineral* 39:231. 1954.
35. McBain, J. W. Sorption of Gases and Vapors by Solids. Gorge Routledge and Sons, Ltd., London. 1932.
36. Mooney, R. W., Keenan, A. G. and Wood, L. A. Adsorption of Water Vapor by Montmorillonite. I. Heat of Desorption and Application of B. E. T. Theory. *J. Amer. Chem. Soc.* 74:1367-1371. 1952.
37. Mooney, R. W., Keenan, A. G. and Wood, L. A. Adsorption of Water Vapor by Montmorillonite. II. Effect of Exchangeable Ions and Lattice Swelling as Measured by X-Ray Diffraction. *J. Amer. Chem. Soc.* 74:1371-1374. 1952.
38. Mortland, M. M. Adsorption of NH_3 by Clays and Mach. *Soil Sci.* 80:11-18. 1955.
39. Nelson, R. A. and Hendricks, S. B. Specific Surface of Some Clay Minerals, Soils, and Soil Colloids. *Soil Sci.* 56:285-296. 1943.
40. Orchiston, H. D. Adsorption of Water Vapor. I. Soils at 25°C . *Soil Sci.* 76:453-465. 1953.
41. Orchiston, H. D. Adsorption of Water Vapor. III. Homoionic Montmorillonite at 25°C . *Soil Sci.* 79:71-78. 1955.
42. Orchiston, H. D. Adsorption of Water Vapor. IV. Characterization of Expanding Lattice Minerals at 25°C . *Soil Sci.* 79:221-224. 1955.
43. Pauling, L., Wood, R. D. and Studivoant, J. H. An Instrument for Determining the Partial Pressure of Oxygen in Gas. *J. Amer. Chem. Soc.* 68:795-798. 1946.
44. Penman, H. Gas and Vapor Movements in the Soils. I. The Diffusion of Vapors Through Porous Solids. *Jour. Agr. Sci.* 30:437-462. 1940.
45. Penman, H. Gas and Vapor Movements in the Soils. II. The Diffusion of Carbon Dioxide Through Porous Solids. *Jour. Agr. Sci.* 30:570-581. 1940.

46. Quirk, J. P. Significance of Surface Areas Calculated from Water Vapor Sorption. Isotherms by Use of the B. E. T. Equations. *Soil Sci.* 80:423-433. 1955.
47. Randall, M. and Farley, G. F. The Activity Coefficients of Gases in Aqueous Salt Solutions. *Chem. Rev.* 4:271-284. 1927.
48. Raney, W. A. Field Measurement of Oxygen Diffusion Through Soil. *Soil Sci. Soc. Am. Proc.* 14:61-63. 1949.
49. Richards, L. A. and others. Diagnosis and Improvement of Saline and Alkali Soils. U. S. Dept. Agr. Handbook No. 60. 1954.
50. Russell, H. J. and Appleyard, A. The Atmosphere of the Soil: Its Composition and the Causes of Variation. *Jour. Agr. Sci.* 7:1-48. 1915.
51. Simmons, C. F. The Effect of Carbon Dioxide Pressure upon Equilibrium of the System: Hydrogen Colloidal Clay - H_2O - $CaCO_3$. Unpublished Ph.D. Thesis. Columbus, Ohio, Ohio State University Library. 1937.
52. Smith, F. B. and Brown, P. E. Diffusion of Carbon Dioxide Through Soils. *Soil Sci.* 35:413-423. 1933.
53. Soto, C. Chemical Studies of the Surfaces of Clay Minerals. 1. Sorption of Ammonia and Methanol by Bentonite. 2. The Effect of Heat Treatment on the Subsequent Sorption of Gases by Bentonite. *Clay Mineral Bul.* 2. 1954.
54. Taylor, G. S. and Abrahams, F. H. A Diffusion Equilibrium Method of Obtaining Soil Gases under Field Conditions. *Soil Sci. Soc. Am. Proc.* 17:201-206. 1953.
55. Taylor, S. A. Oxygen Diffusion in Porous Media as a Measure of Soil Aeration. *Soil Sci. Soc. Am. Proc.* 14:55-61. 1949.
56. Truesdale, G. A., Downing, A. L. and Lowden, G. F. The Solubility of Oxygen in Pure Water and Sea-Water. *Jour. Applied Chem.* 5:53-62. 1955.

57. Van Bavel, C. H. M. A Soil Aeration Theory Based on Diffusion. Soil Sci. 72:33-46. 1951.
58. Whipple, G. C. and Whipple, M. C. Solubility of Oxygen in Sea Water. J. Am. Chem. Soc. 33:362-365. 1911.
59. Wiebe, R. and Gaddy, V. L. The Solubility of Helium in Water and O₂, 25, 50, and 75° and at Pressures to 1000 Atmospheric. J. Am. Chem. Soc. 57:847-851. 1935.

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