

1934

Oxidation-reduction potentials and their application to soils

Matthew Cotton Darnell
University of Massachusetts Amherst

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OXIDATION-REDUCTION POTENTIALS
AND THEIR APPLICATION TO SOILS

DARNELL, JR. 1934

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Oxidation-reduction Potentials
and
their Application to Soils

by

Matthew Cotton Darnell, jr.

Thesis submitted for degree of Master of Science

Massachusetts State College, Amherst

June 1, 1934

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I. INTRODUCTION

Since Gillespie (5)[⊗], in 1920, first measured the potential in a soil, using an indifferent electrode, numerous investigations have been made concerning the methods of measuring this oxidation-reduction potential. Several soil properties have been shown to be empirically associated with the potential, and numerous soil phenomena have been claimed, but not demonstrated, to be resultant from high or low potentials. For the most part, these investigations have been concerned with the methods of determination and the effects of artificial changes on the value of the potentials. There is a need for more fundamental study of the cause-effect relationships of the oxidation-reduction potential to other soil properties.

In the literature of soil science, there is no explanation of the significance of oxidation-reduction potentials in general; and the fact that there are, in current use, two conventions for the designation of potentials, each leading to values opposite in sign, makes the interpretation of the results reported in the literature practically impossible by the average reader. In textbooks of physical chemistry the situation is equally complicated, since the authors who give the most complete explanations of oxidation-reduction potentials differ as to the use of the convention.

This paper, then, has been undertaken with two purposes in mind:

- (1) To assemble the chief theoretical principles of

[⊗] References by number to "Literature Cited".

oxidation-reduction potentials in terms of one convention, and to explain the chemical significance of potentials designated in terms of that convention.

(2) To report an attempt to demonstrate these principles in a specific oxidation-reduction system of the soil.

II. HISTORY AND GENERAL APPLICATIONS OF OXIDATION-REDUCTION POTENTIALS

A. History

In 1898, Peters (11) derived an equation for the oxidation-reduction potential^② of a system, in which equation he showed that the potential varies with the concentrations of the reacting substances. In his experimental work, he showed that his equation was valid for the ferrous-ferric system.

Since Peters' research was done, the concept of oxidation-reduction potentials has come into wide use in theoretical and practical chemistry and in biology.

B. Applications to Chemistry

Oxidation-reduction potentials are used in theoretical chemistry in the formulation of galvanic cells, from which energy relationships and equilibrium phenomena may be calculated. In practical chemistry the understanding of oxidation-reduction potentials has led to many refinements in quantitative analysis, notably in hydrogen-ion determination, electrolytic analysis,

^②Throughout this paper, the terms "oxidation-reduction potential" and "potential", and the symbol " E_h ", have been used interchangeably.

and electrometric titration.

C. Applications to Physiology and Bacteriology

In physiology, great significance has been attached to the oxidation-reduction potential in studying the mechanism of respiration and of cell metabolism. In fact, several physiological systems have been found to behave as purely chemical oxidation-reduction systems, for instance: the cystine-cysteine system, the glutathione system, the haemoglobin systems, and various cell pigment systems. Michaelis (10) has given an excellent review of these systems, and has noted several ingenious methods for their measurement.

Similarly, this property of substances is being studied from the standpoint of bacteriology. Allyn and Baldwin (1) found that the oxidation-reduction potential of a culture medium determines, to some extent, the ability of specific organisms to grow on the medium and that certain organisms are able to change the potential of a poorly poised medium. They also found (2) that a limited oxygen supply resulted in a lowering of potential, probably from oxygen depletion, and that the behavior of Rhizobia toward atmospheric oxygen seems to be governed by the oxidation-reduction potential of the medium. Miss Heintze (6), without mentioning her authority, states that in standardized media the rate of denitrification can be correlated with changes of potential.

D. Applications to Agronomy: Review of Literature

1. The findings of different investigators

The first investigation of the oxidation-reduction potential of soils was carried out by Gillespie (5), who found that strong negative potentials were developed in soils treated with an excess of water; that the rate of decrease of potential varied widely with different soils; and that the addition of 0.1 per cent of dextrose to the soil before moistening resulted in even lower potentials.

Remesow (12) working on Russian podzols, found that as soils approached swampy conditions, the potentials decreased. From a periodic examination of field soils he found that the potentials were higher during the first half than during the last half of the summer. His experiments on newly cultivated podzols showed decreases of potential on fields which had received treatments of stable manure, and increases of potential on those which had received treatments of lime and manure five years previously. The latter treatment, he stated, resulted in stimulation of chemical and biochemical oxidation processes.

Herzner (7) ran a systematic study of the oxidation-reduction potentials of different Austrian soils, to find the best method for the determination of potentials in soils, and to find the relationship of the potential to other soil properties. He showed that the potential of a soil was a direct function of its hydrogen-ion concentration. He was able to demonstrate no appreciable effect of manures on the potential.

Willis (14) showed that liming certain soils to pH 6.2 caused manganese deficiency chlorosis in plants grown on it. He claimed, but did not demonstrate, that this was due to increased reductiveness at higher pH values. The same author (15) later

showed that the E_h of a poorly drained, sandy soil, rich in organic matter, varied inversely with the pH, and stated that liming should be gauged with reference to increased reductiveness at high pH's. In another paper (16) he attributed the potential primarily to hydrogen ion concentrations, but offered the idea that changes may be caused by oxygen depletion, due to either bacterial activity or oxidation of organic matter.

Brown (3) studied 70 methods of determining the oxidation-reduction potentials of soils, and devised from his data his concept of an ideal method.

Miss Heintze (6) found that in a large number of English soils the E_h showed an inverse relationship to the pH; that a blue-grey water-logged soil differed, for similar pH values, from a highly oxidizing tropical soil less markedly than did the E_h 's of adjacent experimental plots of the same pH; and that a water-logged gley soil containing a considerable quantity of iron in the ferrous state had a moderately high E_h . She agreed with Herzner that manures have a very slight, if any, effect on the E_h of a soil. However, she observed appreciable differences in soils of high organic matter content. She stated that the E_h of a soil is of no significance as a measure of its reducing power, except when the pH of the soil is known. In the laboratory, she found a marked drop in potential after several days, due to the water-logging of soils which were known to contain organic matter capable of rapid aerobic decomposition.

2. Methods of determination of the potentials of soils

Each of the above named soil investigators used a

different technique in the determination of the soil oxidation-reduction potential.

Gillespie saturated a 200 g. portion of soil with water, packed the resulting soil paste around the electrode, inserted a salt bridge at various time intervals, and measured this half-cell against a standard electrode. He removed the portion of soil contaminated by the bridge after each measurement.

Remezow made a 1:1 soil-water suspension, allowed this to stand fifteen-eighteen hours, inserted 2 platinized platinum electrodes, allowed them to stay in contact overnight, and read the potential.

Herzner's recommended method consisted of placing the soil in a Gooch crucible, setting this in a pan of water, inserting a bright platinum electrode when the water appeared at the surface of the soil, and reading within an hour.

Willis shook a 1:1 soil-water suspension in an open flask for three days, transferred this to a special flask, and read duplicate bright platinum electrodes in an atmosphere of nitrogen at reduced pressure, after 25 minutes of soil-electrode contact.

Brown inserted a bright platinum electrode into a 7:4 soil-water suspension, and after 30 minutes contact, centrifuged the suspension for 5 minutes and read the potential.

Miss Heintze read the potential of a glass electrode in a 1:1 soil-water suspension in 1-2 hours.

Experiments of Herzner and Miss Heintze, and the statement of Michaelis (10), indicated that displacement of

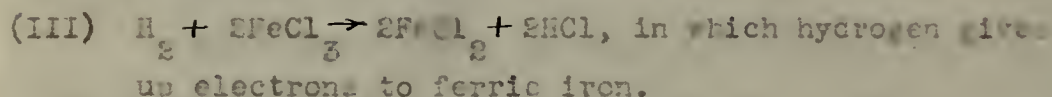
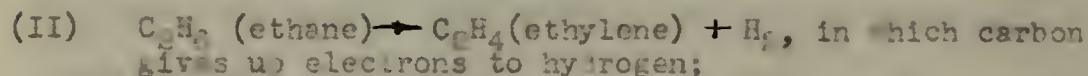
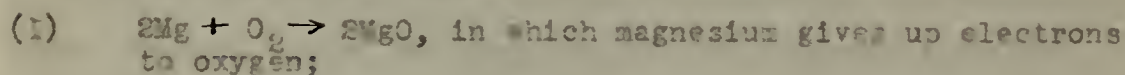
oxygen in the system is not necessary with bright platinum electrodes.

III. THE THEORY OF OXIDATION-REDUCTION POTENTIALS, AND EXPERIMENTAL STUDY

A. Theoretical Considerations

1. Definitions

According to present understanding, oxidation is any chemical process involving the loss of electrons by an atom. This may be accomplished by combination with oxygen, by the loss of combined hydrogen, or by the loss of electrons to another atom. These three types of oxidation may be illustrated by the following equations:



Conversely, reduction consists of the gain of electrons by an atom. In the above equations oxygen, hydrogen, and ferric iron, respectively, are reduced.

The term oxidant signifies a substance which can oxidize, or take up electrons from, another substance. The term reductant signifies a substance which can reduce, or give up electrons to, another substance.

2. The general equation for oxidation-reduction potentials

The physical chemist measures the "driving force" of a chemical reaction by the amount of energy released to

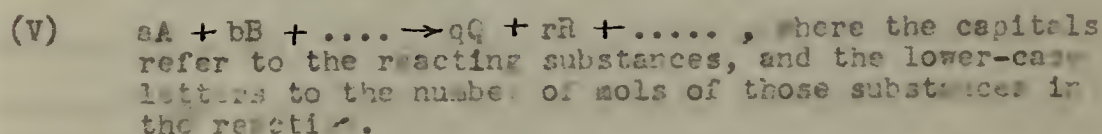
surrounding systems or containers when the designated change takes place. Thus, if a sheet of zinc is dipped into a beaker of dilute sulphuric acid, energy is manifested in the expansion of the evolved hydrogen gas and in the warming of the reaction mixture. In so crude an apparatus, it would be impossible to convert all the released energy into useful work. There would be frictional losses in the harnessing of the gas, losses in heat to the surrounding matter, and eventual cessation of the reaction due to polarization.

However, if a galvanic cell be constructed of the reacting substances, and allowed to discharge at infinitesimally low current, while the temperature and pressure are kept constant, the energy loss or "free energy" is converted quantitatively into work.

Under these ideal conditions, then, the "driving force", or "maximum obtainable work", W_e , is equal to the energy loss or "free energy decrease", $-\Delta F$. Or,

$$(IV) \quad W_e = - \Delta F$$

Let us consider a general example of a galvanic cell, in which the passage of N equivalents of electricity causes the reaction below to take place:



The equation for the change of free energy of such a system, at constant temperature and pressure, becomes, on integration,

$$(VI) \quad \Delta \mathcal{F} = \Delta \mathcal{F}_0 + RT \ln \frac{(Q)^q (R)^r \dots}{(A)^a (B)^b \dots}, \text{ where } \Delta \mathcal{F} \text{ is the change of free energy accompanying the change indicated in equation (V); } \Delta \mathcal{F}_0 \text{ is the change of free energy when each of the reacting substances is at unit activity}^{\otimes}; R \text{ is the gas constant, } 8.315 \text{ joules; } T \text{ is the absolute temperature, } 273.1 + \text{centigrade temperature; } (Q), (R), (A), (B), \text{ etc. are the activities of the reacting substances; } \ln \text{ is the symbol for "natural logarithm", } \ln a = 2.303 \log_{10} a.$$

Now electrical work, in joules, may be stated as the product of the number of equivalents, N , the coulombs per equivalent, F , and the electromotive force, E . So the maximum electrical work of any reaction is

$$(VII) \quad W_e = NEF$$

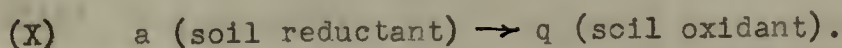
Combining equation (IV) and (VII),

$$(VIII) \quad -\Delta \mathcal{F} = NEF$$

On substitution of $-NEF$ for $-\Delta \mathcal{F}$, and simplification, equation (VI) becomes

$$(IX) \quad E = E_0 - \frac{RT}{NF} \ln \frac{(Q)^q (R)^r \dots}{(A)^a (B)^b \dots}, \text{ where } E_0 \text{ is the potential when the substances are at unit activity.}$$

As a special case, we may consider a reversible mixture of a soil oxidant and soil reductant, in which the passage of N equivalents of electricity causes the following change:



General equation (IX) then becomes:

[⊗] Activity is, in dilute solutions, approximately proportional to the concentration. In this paper, the conventional symbol (Q) for the activity of any substance, such as Q , has been used.

$$(XI) \quad E = E_0 - \frac{RT}{nF} \ln \frac{(\text{soil oxidant})^q}{(\text{soil reductant})^a}$$

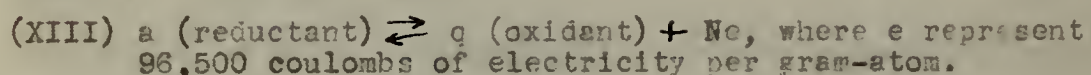
E , or as it is generally written, E_h , is the oxidation-reduction potential of the system when the oxidant is at the activity (ox) and the reductant is at the activity (red). In so complex a mixture as a soil solution, E_0 and n are, for practical purposes, indeterminate.

Equation (XI) is important, however, in that it shows the relationship of the measured potential to the activities (concentrations) of the oxidant and reductant.

The general equation for oxidation-reduction potentials,

$$(XII) \quad E_h = E_0 - \frac{RT}{nF} \ln \frac{(\text{ox})^q}{(\text{red})^a},$$

is applicable to any oxidation-reduction system of the form,



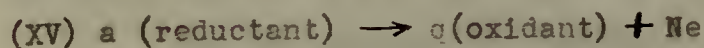
3. The sign of oxidation-reduction potentials

Throughout this discussion the convention of Lewis and Randall (9), concerning the sign of potentials, has been adhered to. According to this convention, a positive potential is a measure of the tendency of negative electricity to pass spontaneously, from right to left, through the half-cell,[⊗]

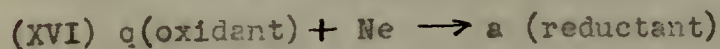


[⊗] This is the conventional method of formulating a half-cell; "Pt" refers to any inert metal, and "ox" and "red" refer respectively to the oxidant and reductant, into a solution of which the inert metal dips.

In other words, a positive potential measures the tendency of equation (XV) to proceed from left to right.



If we consider the reverse equation,

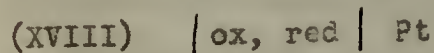


the equation for its potential becomes

$$(XVII) \ E_n = E_o - \frac{RT}{nF} \ln \frac{(\text{red})a}{(\text{ox})^q};$$

however, conventional texts always state the potential as that of the equation in the form of (XV).

A system which proceeds spontaneously in the direction of equation (XVI), then, has a negative tendency to proceed in the direction of equation (XV). Consequently, negative electricity flows spontaneously through half-cell (XIV) from left to right, or through half-cell

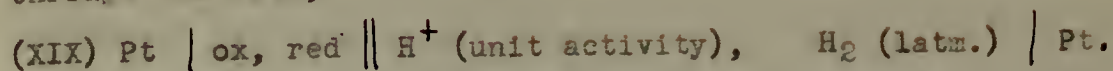


from right to left. Consequently, a system proceeding in the direction of equation (XVI) has a negative potential in the half-cell of the form of (XIV), and a positive potential in the half-cell of the form of (XVIII).

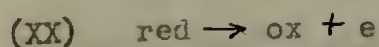
4. The chemical significance of potentials

The magnitude of an oxidation-reduction potential is a relative term. As an arbitrary standard, the potential of the hydrogen half-cell, at one atmosphere of hydrogen pressure, unit hydrogen-ion activity, and 25°C. temperature, has been taken as .0000 volt. Any oxidation-reduction potential may then be defined as the tendency of negative electricity to pass

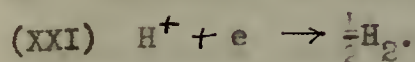
through the cell,



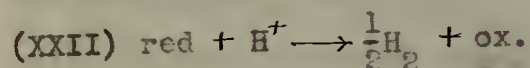
Let us combine the equations for the two electrode reactions of cell (XIX),



and



On addition,

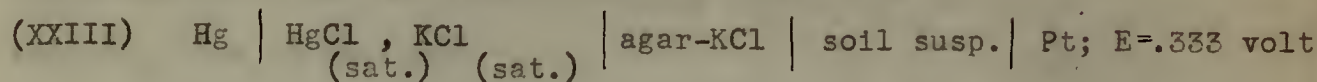


If cell (XIX) has a positive potential, and the unknown potential, consequently, a positive value, then reaction (XXII) proceeds in the indicated direction. This may be interpreted to mean that the system is more reducing than hydrogen at 1 atmosphere of pressure in a solution of pH 1. A negative value of the potential, then, would mean that the system is less reducing than hydrogen under these conditions.

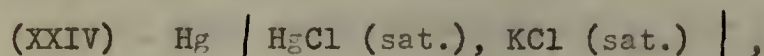
5. The measurement of potentials

The measurement of oxidation-reduction potentials consists of constructing a galvanic cell, of which one electrode is a "standard half-cell" and the other is an inert metal dipping into the solution of unknown potential. This cell, which has two electrodes of different potentials, gives rise to an e.m.f. (which, by definition, is a difference of potential). The e.m.f. of the cell is balanced in a potentiometer (plate I, fig.2) by an equal, oppositely directed e.m.f., whose magnitude

is measured. The potential of the "standard half-cell" is subtracted from the e.m.f. of the whole cell to give the unknown potential. For example, let us take the cell



The above cell designation indicates that the cell has an e.m.f. of $+ .333$ volt, so negative electricity must pass spontaneously from right to left. (The standard half cell is connected to the "-" potentiometer pole). In a table of potentials, the value of the potential of the "standard half cell", in this case the saturated calomel electrode,



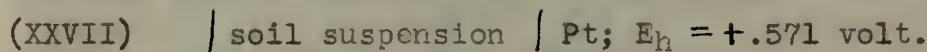
is given as $-.238$ volt at 35°C . Now the e.m.f. of the cell is equal to the sum[⊗] of the potentials of its half-cells, or

$$(XXV) \quad E_{\text{cell}} = E_h + E_{\text{standard half-cell}}.$$

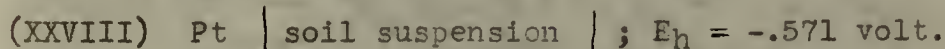
Transposing, and substituting,

$$(XXVI) \quad E_h = .333 - (-.238).$$

Hence we may evaluate the oxidation-reduction potential of the soil half-cell, as written,

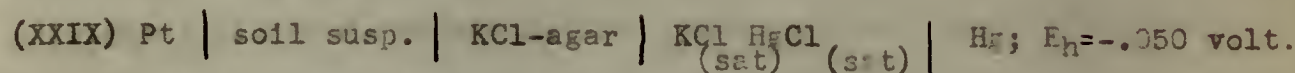


Or, to follow the convention, the potential of the half-cell



⊗ If we follow the convention of Lewis and Randall, we must use the sum rather than the difference of potentials. This apparent discrepancy is corrected in the measurement of the tendency of negative electricity to pass through each half-cell as written in cell (XXIII), and in the use of the algebraic values of the potentials. This can be more clearly seen from the text which follows.

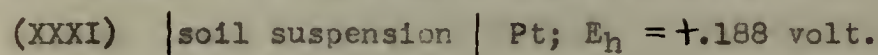
If the total potential of the cell is less than .000 volt, the poles of the cell must be reversed on the potentiometer. The measured potential would then be, for example, that of the cell



This gives to the potential a value of



For comparison with (XXVII), the potential of

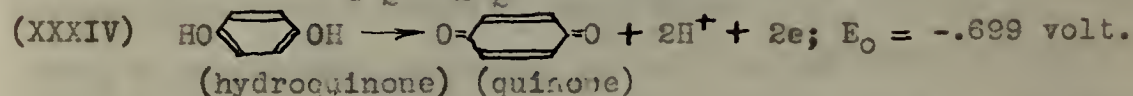
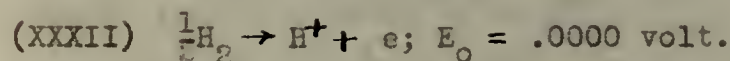


is used.

Such positive values of E_h for a half-cell arranged as (XXVII) or (XXXI) indicate that such oxidation-reduction systems will be reduced by hydrogen at the conditions specified for cell (XIX).

6. Important single oxidation-reduction systems

Perhaps the three most interesting oxidation-reduction systems, to the soil scientist, are these:



The hydrogen system, (XXXII), is the basis of the hydrogen electrode, which has been widely used in all electro-metric work. The hydrogen electrode is generally made up of an adsorptive metal, such as black platinum, saturated with

hydrogen gas at a known pressure, dipping into an acid solution of known hydrogen-ion concentration. From its specific oxidation-reduction formula,

$$(XXXV) \quad E_h = - \frac{RT}{nF} \ln \left(\frac{H^+}{p} \right)^{1/2}, \text{ where } p \text{ is the hydrogen pressure,}$$

its potential can be calculated and used as a reference potential.

Due to the difficulty of establishing equilibrium, the oxygen system, (XXXIII), is not used as a reference electrode. This system owes its importance to the fact that it sets the lower limit of potentials which can be measured in aqueous solution. The hydrogen system, likewise, sets the upper limit of measurable potentials in water.

The specific potential formula of the oxygen electrode is:

$$(XXXVI) \quad E_h = -.39 - \frac{RT}{F} \ln \frac{p^{1/2}}{(OH)^-}, \text{ where } p \text{ is the oxygen pressure.}$$

Let us calculate E_h for different values of (H^+) in equations (XXXV) and (XXXVI), remembering that in aqueous solution, $(H^+) \times (OH^-) = K = 10^{-14}$ (K is the dissociation constant). We can then see that the potential of the hydrogen electrode varies logarithmically with (H^+) , from .000 volt at $(H^+) = 1$, to +.83 volt at $(H^+) = 10^{-14}$, if the hydrogen pressure is kept at one atmosphere. Similar calculations for the oxygen electrode shows a logarithmic variation in E_h from -.39 volt at $(OH^-) = 1$, $(H^+) = 10^{-14}$, to -1.23 volts at $(OH^-) = 10^{-14}$, $(H^+) = 1$. Calculated values for the E_h of the hydrogen electrode, at decreased pressure, show a uniform decrease, over the whole pH range, of .12 volt for each pressure decrease by 10^{-1} . Likewise, the E_h of the oxygen

electrode increases .06 volt for a decrease of oxygen pressure by 10^{-4} .

The importance of these facts is that at any given pH, the H^+ or OH^- ions in the aqueous solution of an oxidation-reduction system will establish a definite oxygen or hydrogen pressure, depending on the oxidation-reduction potential of the system. In a large number of systems, it has been found that such oxygen or hydrogen pressures are so small that they are negligible, and do not readily establish equilibrium with the electrode metal. But, as a general rule, potentials of aqueous oxidation-reduction systems cannot be measured with any accuracy unless they lie between the potentials of the oxygen and hydrogen electrodes at the pH of the solution. For at a pH of 1, for example, a system having an E_h of less than -1.23 volts, would develop oxygen from water, but only to a pressure of slightly greater than atmospheric pressure. This oxygen pressure would not be sufficient to give a definite potential under such conditions. The potential of such a solution is said to lie in the region of "oxygen overvoltage".

The quinhydrone system (XXXIV) is known to practically all soil investigators. But not every one knows just what relationship the oxidation-reduction potential of the quinhydrone system bears to pH.

Quinhydrone is an equimolecular mixture of quinone and its reduction product, hydroquinone. When it is introduced into water, it forms an equimolecular mixture of oxidant and reductant.

From equation (XXXIV) it can be seen that

$$(XXXVII) E_h = -.699 - \frac{RT}{2F} \ln \frac{(\text{quinone}) (H^+)^2}{(\text{Hydroquinone})}$$

or

$$(XXXVIII) E_h = -.699 - \frac{RT}{2F} \ln \frac{(\text{quinone})}{(\text{Hydroquinone})} - \frac{RT}{F} \ln (H^+)$$

But since (quinone) = (hydroquinone), the ratio of these activities is 1, and $\ln 1 = 0$, so the second term drops out.

Hence,

$$(XXXIX) E_h = -.699 - \frac{RT}{F} \ln (H^+).$$

Since $pH = \log \frac{1}{(H^+)}$, we may write

$$(XL) E_h = -.699 + 2.303 \frac{RT}{F} (pH)$$

Rearranged, equation (XXXIX) becomes

$$(XLI) pH = (.699 + E_h) \left[\frac{F}{2.303RT} \right]$$

Equation (XL) shows the direct relationship between the pH, or the H^+ ions, in a solution to the oxidation-reduction potential shown by quinhydrone in that solution. It is unfortunate that in solutions more alkaline than pH 8.25, hydroquinone is appreciably ionized, yielding H^+ ions which destroy the usefulness of the system in pH determinations in this range.

7. Mixtures of oxidation-reduction systems.

In so heterogeneous a phase as a soil solution there are certain to be several oxidation-reduction systems present. Hence, a few aspects of mixtures of oxidation-reduction systems are presented here.

A series of reversible oxidation-reduction systems, when mixed, will establish an equilibrium at a definite potential. This equilibrium potential will be determined by the relative concentrations of, and the potentials of, all systems present. When this definite potential is established, each system of lower E_0 having a relatively low concentration of (ox)+(red), will be practically all reduced. In general, the final potential of the mixture will be determined by the concentrations of (ox) and (red) in those systems having the greater total concentrations of (ox) + (red).

The poise, or resistance to change of potential, of an oxidation-reduction system becomes greater with increasing concentrations of (ox) + (red). For any given total concentration of (ox) + (red), the poise is greatest when the ratio, (ox):(red), equals 1.

If equimolecular mixtures of different strong oxidants are added to an excess of another oxidation-reduction system, they will oxidize it to the same degree, giving the same final potential. Only a very slight excess of a strong oxidant (that is, an oxidation-reduction system of high E_0 , which is practically all oxidized), need be added to an equimolecular quantity of another system, to bring about practically complete oxidation of the latter system. This is the principle of electro-metric titration.

8. Sources of information

The above discussion is a compilation of the theory

as derived in part by Clark (4), by Michaelis (10), and by Lewis and Randall (9). As these authors use different approaches to the problem, and different conventions for the formulation of potentials, it was considered desirable to assemble, in terms of one derivation and one convention, the three phases which are equally important to the complete understanding of the subject. The convention of Lewis and Randall for the designation of potentials has been chosen because it is coming into predominant use among the American chemists.

B. Experimental

1. Object of the experimental work

In the above discussion, it has been shown that the oxidation-reduction potential of a system depends on the concentrations of its oxidant and reductant, and that in a mixture of systems, the potential will be determined chiefly by those systems having the greater total concentrations of oxidant plus reductant.

Of all the oxidation-reduction systems in the soil,-- such as carbonaceous materials- CO_2 ; $\text{NH}_3\text{-NO}_3^+$; $\text{OH}^- \text{-O}$; $\text{H}_2\text{-H}^+$; $\text{Fe}^{++}\text{-Fe}^{+++}$; $\text{Mn}^+\text{-Mn}^{++}$; $\text{S}^- \text{-S}$; and S-SO_4^{++} , -- the most important, from an agronomic point of view, are the carbon, nitrogen, and hydrogen systems. The relationship of the reversible hydrogen system to the oxidation-reduction potential has already been established. That the carbon system is reversible has not been demonstrated. But Latimer and Hildebrand (8), in a table of potentials, indicate that the ammonia-nitrate system is reversible, and has a definite potential at given concentrations. The unauthorized statement of Miss Heintze (6), that "in standardized media the form of the potential-time curve can serve to characterize groups of microorganisms or cellular processes, e.g., denitrification" leaves the conclusion to be drawn that the nitrogen system, present in great enough concentration, should play a major part in the determination of the potential of a soil.

It is a general opinion that biochemical processes proceed at a slower rate than do purely chemical ones. Now

a review of the literature has revealed only one study of soil oxidation-reduction potentials as they vary over a period of weeks; that study represents an empirical study of potentials, rather than an analytical study of the causes of changes of potential.

The place is well established for an analytical study of soil oxidation-reduction potentials from the standpoint of significant changes in the concentrations of reversible oxidation-reduction systems.

The object, therefore, of this experiment has been

(1) to study the changes in the oxidation-reduction potentials of different soils, over periods of time long enough to permit biological activity to cause significant changes in the nitrogen system; and thereby to ascertain if the nitrogen system plays a part in the determination of the potentials of soils; and

(2) to note any changes in the oxidation-reduction potentials which may be ascribed to soil acidity, soil type, or fertilizer treatment.

2. Procedure

Various soils were limed at abnormally high rates, and different forms of nitrogen were applied. Periodic analyses of nitric and ammoniac nitrogen, pH, and E_h were made over an 8-weeks' course of nitrification in the greenhouse. These four measurements were plotted on the same chart for each

soil, taking $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$ pH, and E_n as ordinates against times as abscissas.

a. Soils used

- 1- A well-drained sandy loam pasture soil from the lower Brooks' farm, M.S.C.
- 2 - The same soil in a natural water-logged condition, showing the growth of sedges.
- 3 - A gravelly sand, taken from the railroad fill on Tillson farm, M.S.C.
- 4 - A black, sandy soil taken from the swamp on Tillson farm, M.S.C.

b. Treatment of soils.

About 400 pounds of each soil, in its natural condition, were collected Jan. 9, 1934. After the soils had dried for two or three weeks, the clods were broken up and the samples were sifted twice through a 3-mesh sieve. The samples were mixed several times, and divided into two parts. To one was added $7\frac{1}{2}$ tons per acre of lime [58 per cent Ca(OH)_2 , 41. per cent CaCO_3]; to the other was added no lime. The limed portions were again thoroughly mixed. One week later, both the limed and the unlimed portions were again subdivided into four 8 kg. parts each. Nitrogen treatments were then applied as explained in table 1. After the nitrogen treatments were applied, the 32 resulting portions were thoroughly mixed and placed, to a depth of about four inches, in wooden boxes one foot square by six inches deep. The boxes were so constructed as to leave a quarter-inch opening along the bottom, which was

covered with a paper towel.

The boxes were placed on a greenhouse bench and watered at least once a week. As this experiment was primarily concerned with the changes of oxidation-reduction potential, no attempt was made to maintain optimum moisture conditions for nitrification.

Samples were taken at the time of nitrogen applications and at approximate two-weeks' intervals, for the determination of moisture, $\text{NO}_3\text{-N}$, $\text{NH}_3\text{-N}$, pH, and E_h .

Table 1

Treatment of soils

Soil	Description	Lime Applied ^{a, b}	Nitrogen applied ^a
100	Well drained, fine sandy loam, from Brooks' Farm, M. S. C.	None	None
101		None	30.mgm. $\text{NH}_3\text{-N}$ per 100.g. soil
102		None	1.0g.dried blood per 100.g.soil
103		None	30. mgm. $\text{NO}_3\text{-N}$ per 100.g. soil
110		7 $\frac{1}{2}$ tons/acre	None
111		7 $\frac{1}{2}$ tons/acre	30.mgm. $\text{NH}_3\text{-N}$ per 100.g. soil
112		7 $\frac{1}{2}$ tons/acre	1.0g. dried blood per 100.g.soil
113		7 $\frac{1}{2}$ tons/acre	30.mgm. $\text{NO}_3\text{-N}$ per 100.g. soil
200	Poorly drained, fine sandy loam, from Brooks' Farm, M. S. C.	None	None
201		None	30.mgm. $\text{NH}_3\text{-N}$ per 100.g. soil
202		None	1.0g.dried blood per 100.g.soil
203		None	30.mgm. $\text{NO}_3\text{-N}$ per 100.g. soil
210		7 $\frac{1}{2}$ tons/acre	None
211		7 $\frac{1}{2}$ tons/acre	30.mgm. $\text{NH}_3\text{-N}$ per 100.g. soil
212		7 $\frac{1}{2}$ tons/acre	1.0g. dried blood per 100.g.soil
213		7 $\frac{1}{2}$ tons/acre	30.mgm. $\text{NO}_3\text{-N}$ per 100.g. soil
300	Gravelly sand fill, from Tillson Farm, M. S. C.	None	None
301		None	30.mgm. $\text{NH}_3\text{-N}$ per 100.g. soil
302		None	1.0g.dried blood per 100.g.soil
303		None	30.mgm. $\text{NO}_3\text{-N}$ per 100.g. soil
310		7 $\frac{1}{2}$ tons/acre	None
311		7 $\frac{1}{2}$ tons/acre	30.mgm. $\text{NH}_3\text{-N}$ per 100.g. soil
312		7 $\frac{1}{2}$ tons/acre	1.0g.dried blood per 100.g.soil
313		7 $\frac{1}{2}$ tons/acre	30.mgm. $\text{NO}_3\text{-N}$ per 100.g. soil
400	Black, sandy swamp soil, from Tillson Farm, M. S. C.	None	None
401		None	30.mgm. $\text{NH}_3\text{-N}$ per 100.g. soil
402		None	1.0g.dried blood per 100.g.soil
403		None	30.mgm. $\text{NO}_3\text{-N}$ per 100.g. soil
410		7 $\frac{1}{2}$ tons/acre	None
411		7 $\frac{1}{2}$ tons/acre	30.mgm. $\text{NH}_3\text{-N}$ per 100.g. soil
412		7 $\frac{1}{2}$ tons/acre	1.0g.dried blood per 100.g.soil
413		7 $\frac{1}{2}$ tons/acre	30.mgm. $\text{NO}_3\text{-N}$ per 100.g. soil

a - Applications of lime and nitrogen made on the basis of air dry soil.

b - Liming material analyzed 58% Ca(OH)_2 , 41.5% CaCO_3 .

day. Determinations of pH were made as soon as convenient, never more than four days after sampling.

Moistures were determined by drying 20 gm. portions of the soils at 105°C . for twenty to twenty-five hours.

Determinations of pH were made by the quinhydrone electrode. About 15 gm. of air-dry soil, 0.05 gm. of quinhydrone, and a 1:2 soil-water ratio were used.

Nitrate nitrogen determinations were made colorimetrically by the phenol-disulphonic acid method. Readings were made in the range of 50-100 mm. of 1 p.p.m. standard.

Ammonia nitrogen determinations were made according to Harper's method.

The following method was used in the determinations of oxidation-reduction potentials.

Fifty grams of moist soil were placed in a 250 cc. flask with an equal weight of distilled water. The flask was stoppered and shaken at room temperature (about 23°C .) for $2\frac{1}{2}$ --3 days. The contents of the flask were then transferred to a 250 cc., 3-necked Woulff bottle; two bright platinum electrodes were inserted; and the bottle was placed in a constant-temperature water bath at 35°C . Connection to a saturated calomel half-cell was made with a 3 per cent agar-saturated KCl bridge. Within fifteen minutes of contact of the electrodes with the soil suspension, the potential of the resultant cell,

$\text{Hg} \mid \text{HgCl (sat), KCl} \mid \text{Agar-KCl} \mid \text{soil suspension} \mid \text{Pt}$
 was measured electrometrically on a Leeds and Northrup "Portable Acidity Meter". The duplicate electrodes always checked within

c. Methods of analysis

Mixing was carried out on the original samples by sifting twice through a 3-mesh sieve, followed by two "conical pilings", i.e., putting successive shovelfuls of soil from the perimeter of the pile on the top of another conical pile. Division of samples was effected by putting alternate shovelfuls from the sample into different piles and again mixing these. In the application of lime and nitrogen carriers the weighed portion of soil to receive a particular treatment was subdivided into fifteen or twenty parts, with which the carrier was mixed by piling, and these subdivisions combined and the whole again piled.

The method of sampling for analysis represented a departure from that of the Association of Official Agricultural Chemists. To avoid excessive mixing and irregularities of aeration, which, in small quantities of soil, might cause irregularities in the course of nitrification, one to one-and-a-half pound samples were taken in one spot, to the full depth of the soil. The hole left by the sampling was partly filled by the immediately surrounding soil, and the next bi-weekly sample was taken from another spot. The preparation of the sample for analysis consisted of crushing lumps and mixing by three conical pilings. The analyses were made on this unsieved soil. Nitrogen and moisture determinations were started within ten hours after mixing the sample. Except for that of Feb. 10, determinations of the oxidation-reduction potential were started the same or the following

5 millivolts and generally within a narrower range. Plate I is a diagram of this cell, and of the wiring scheme for the determination.

Between determinations on different soils, the agar bridge was rinsed with saturated KCl; between weekly runs, it was set in saturated KCl to prevent desiccation. Before and after each determination on different soils, the platinum electrodes were rinsed with water, then with alcoholic alkali, alcohol, and water. Between weekly runs, the electrodes were set in distilled water. For directions for the preparation of agar bridges, and for the preparation and care of electrodes, see Clark (4).

The above method for determinations was taken from Willis' (14) method, modified particularly in the omission of the displacement of air with nitrogen, which Herzner (7), Brown (3), and Miss Heintze (6) have shown to be unnecessary.

An experiment conducted by the writer in which the method outlined above was compared with the same method using nitrogen displacement and with the method of Brown (3), showed that the results by this method can be rather well duplicated on different samples of the same soil, and that the displacement of air is not necessary. Results of this experiment are shown in table 2. In testing the necessity of displacement of air, the apparatus shown in plate II was used; the diagram is self-explanatory. The soil was shaken as described above, and transferred to the 100 cc. vial. The stopper, into which the

bridge, electrodes, and tubes had already been fitted, was tightly inserted. The vial was placed in the water bath and the indicated connections were made. The potentials as tabulated in column II, table 2, were read in air after 7 minutes. The vacuum was then turned on for 3 minutes, followed by nitrogen + vacuum for 5 minutes, and vacuum alone for 3 minutes. The potentials as tabulated in column III, table 2, were then read. There was a fair agreement between the method used by the writer and the method of Brown.

Table 2

Comparison of methods of determination of E_h

	I	II	III
Soil	E_h volts	E_h aver. volts	E_h aver. volts
200		.382 ^b .552 .565 .545 .545	.383 ^b .553 .565 .545 .547
210	.473 ^a	.443 .448 .442 .340 ^b .458	.441 .446 .441 .340 ^b .458
300		.545 .557 .544 .568 .569	.548 .564 .544 .540 .582
303	.577 ^a	.574 .575 .575 .575 .457 ^b	.578 .577 .578 .578 .458 ^b
400	.584 ^a	.575 .571 .574 .570 .565	.579 .575 .577 .573 .569
412	.462 ^a	.477 .476 .477 .475 .474	.476 .475 .476 .474 .474

a - Only one set of determinations made by this method.

b - This "poisoned" electrode gave erratic results throughout this experiment; consequently, these values are not included in the averages.

I - Brown's (3) method.

II - The writer's method; potential in air.

III - The writer's method; potential in nitrogen atmosphere.

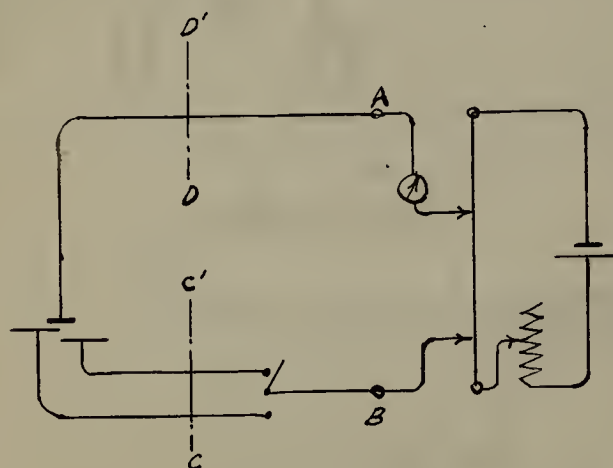
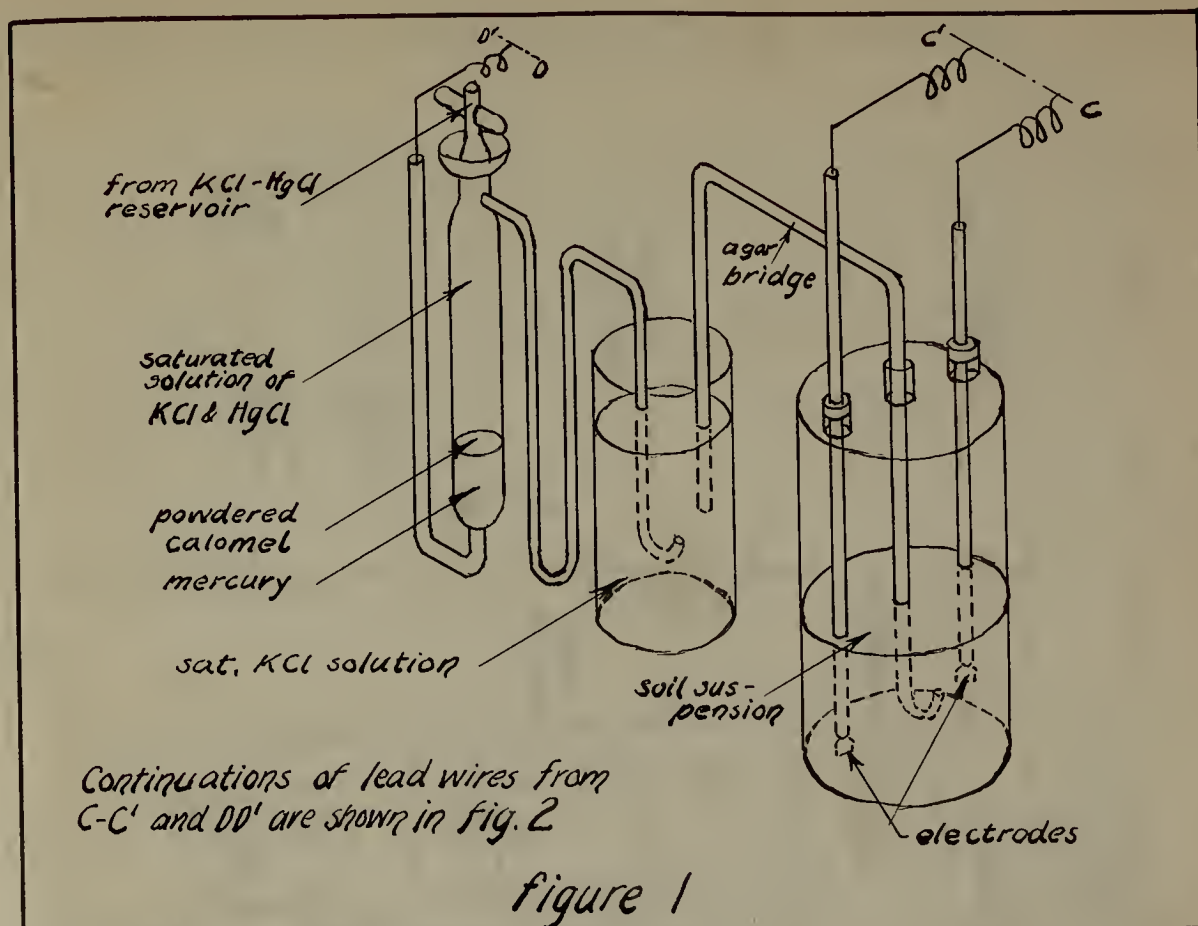


figure 2

PLATE I

figure 1. Oxidation-reduction cell used in routine determinations.
figure 2. Diagram of wiring scheme for potentiometric determination of potentials.

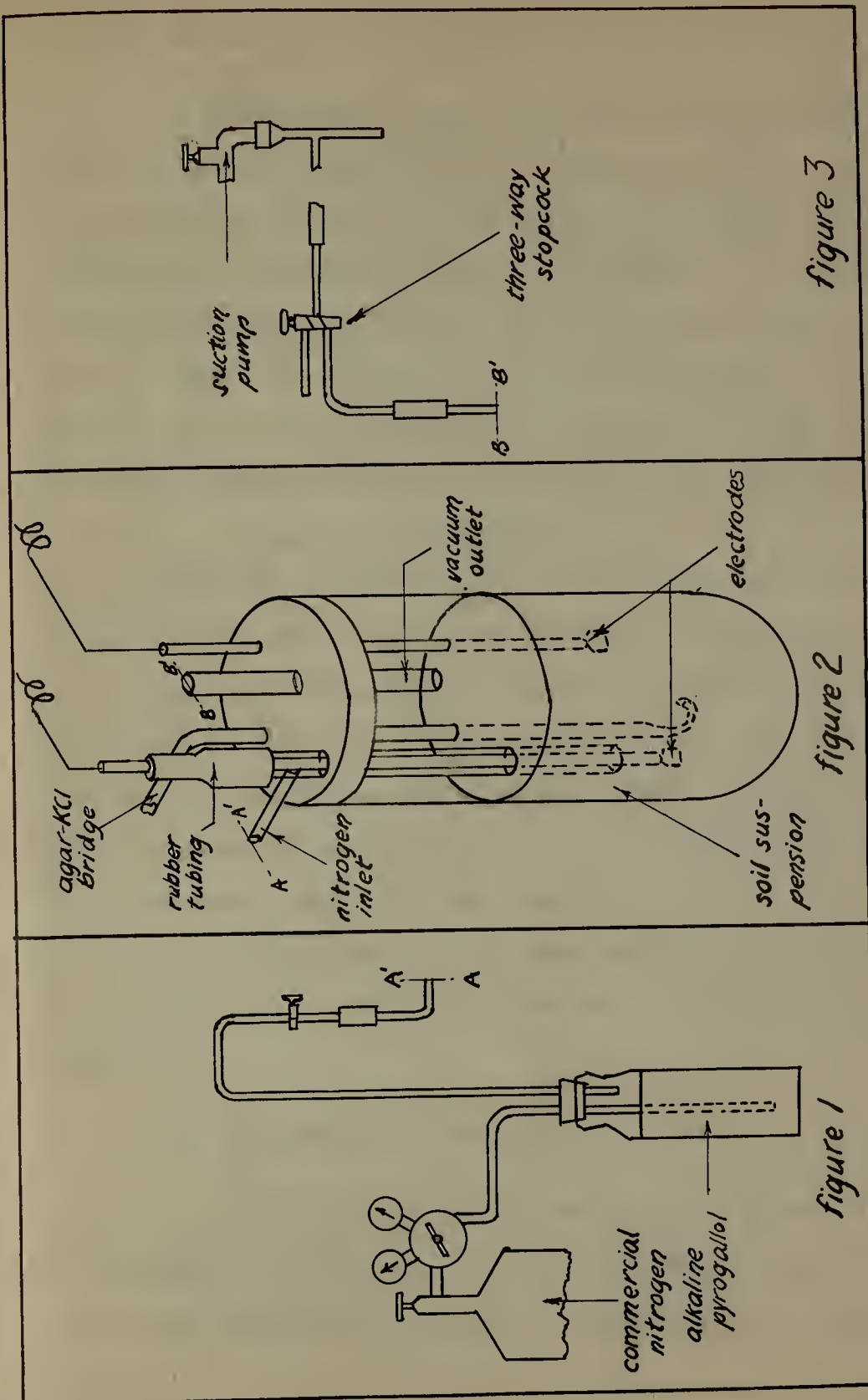


PLATE II

figure 1. Diagram of nitrogen purification train.
 figure 2. Oxidation-reduction half-cell used in comparing methods of determination.
 figure 3. Diagram of vacuum train.

3. Results

A tabulation of the results of this experiment is given in tables 3,4,5,6, and 7. Moistures were calculated as percentages of water in the moist soils. Nitric and ammoniac nitrogen were expressed as parts of nitrogen per million parts of moisture free soil. Acidity was expressed in pH values. Since the values of soil potentials found by the majority of previous investigators seem to indicate that they have been expressed as the potentials of the half-cell,

| soil suspension | Pt,

those potentials observed in this experiment have been expressed in the same manner, for purposes of comparison. It should be remembered that this is not in accord with the convention used in most textbooks, viz., the expression of such potentials as those of the cell above, reversed. However, there is no essential difference as long as it is specified which half-cell is being spoken of, for in either case the interpretation is that the oxidation-reduction system of the soil is more oxidative than the standard hydrogen electrode.

4. Discussion of results

The results given in tables 4, 5, 6, and 7 are shown graphically in charts 1 to 32. Nitrification, changing acidity, soil type, and varied nitrogen treatments were considered

as possible indices of changing potential.

a. Changes of potential with relation to nitrification

Although this experiment was not designed primarily as a nitrification experiment, and progressive increases of nitrate content were not necessarily sought, yet several decreases in the content of nitrate plus ammonia indicated either that the analyses were inaccurate, that there was leaching of nitrates, or that there was active denitrification. It seems reasonable to attribute these losses to leaching and to adsorption of nitrates on the wooden containers.

The charts revealed the following generalities and exceptions.

With the exception of soils numbers 302 and 303, all soils showed a higher E_h at the final than at the initial analysis. In number 302, which was an unlined soil with dried blood treatment, the potential fell off rapidly at first, then rose to almost its original value. The ammonia concentration showed a rapid increase at first, then remained rather constant at a high value. The nitrate concentration showed a slow but steady rise. In number 303, which was an unlined soil with nitrate treatment, there was a rather constant value of the potential until the final determination, when it fell off slightly. The concentrations of ammonia and nitrate changed very little throughout the entire experiment.

The changes in potential were greater in the lined series where nitrification was active, than in the unlined

series where nitrification was slight but ammonification was active. In the lime series all soils showed large changes of potential. In the unlimed series none of those soils to which no nitrogen was added showed large changes. All unlimed soils receiving the dried blood treatment showed large changes of potential, except number 102 in which the rate of nitrification was somewhat proportional to the rate of ammonification.

Similarly, all treatments of unlimed soil number 200 showed large changes of potential except the no-nitrogen treatment in which the changes in the nitrogen system were smaller. The other soils of the unlimed series which showed large changes in potential were numbers 101 and 103, which were ammonium sulphate and the sodium nitrate treatment of soil number 100.

With the exception of one soil, all those showing large changes of potential showed large changes in the nitrogen system. Of those showing small changes in potential, only three showed large changes in the nitrogen system. These were numbers 102, 301, and 401, which were unlimed soils with ammonium sulphate treatments and showed rather rapid ammonification, but little or no nitrification.

In all soils which showed large changes of potential, the changes in the nitrogen system consisted of increased nitrate content at the expense of ammonia content except in several dried blood treatments of numbers 100 and 300. Examination of these exceptions shows that as rapid ammonification took place there was a rapid drop in potential, unless nitrification proceeded at a rate comparable with the ammonification rate. When nitrification was in the ascendancy, as shown by

the decrease of ammonia concentration, the potential again rose. However, soil number 401, in which there was rapid ammonification with no nitrification, disagrees with this generalization.

The increases in potential of those soils which showed no significantly large changes in the nitrogen system were probably due to the changes in other oxidation-reduction systems which were present in greater concentrations, as was explained in the theory of mixtures of oxidation-reduction systems.

In general, since nitrification took place at the expense of ammonia, the nitrate and ammonia curves showed a somewhat inverse trend. Further examination of the data also shows that in general the ammonia and pH curves had the same general trend, and that the nitrate and pH curves had an inverse relationship. Since, according to Herzner (7), Willis (14), and Heintze (6), the E_h is an inverse function of pH, it seems very likely that the apparent direct relationship of nitrate to potential was due to a residual anion effect of nitrification which lowered the pH and consequently raised the potential.

b. Changes of potential with relation to changing acidity

The observations of Herzner, Willis, and Heintze, that the potential is a direct function of acidity were remarkably well verified by the results of this experiment. This relationship held equally well for changes of acidity produced by liming and for those produced, presumably, by microbiological activity.

c. Changes of potential with relation to soil type

Although no determinations were made of the potentials of the soils in their natural conditions of drainage, determinations made after a month of air drying showed no marked differences in potential of soils from widely varying natural conditions. As a rule, however, soil 300, which was a poorly buffered, gravelly sand, showed a slight exaggeration of changes of potential over other soils under similar treatments.

d. Changes of potential due to application of nitrogen carriers

No changes of potential were observed that could be associated with ammonia or nitrate in ammonium sulfate or sodium nitrate. This lack of change confirmed the idea stated above, that the nitrogen system affects a change in potential only as a result of changes within the system which cause changes of acidity.

However, the addition of organic matter, as in the dried blood treatments, and particularly at high pH values, resulted in marked decreases of potential. This was shown particularly well in the cases of soils numbers 402, 319 and 412. In these soils there was a rapid ammonification of the added organic matter in the first two weeks of the experiment, which was interpreted as meaning that the rapid decomposition of organic matter is accompanied by marked decreases of potential.

e. Suggestions for further study

The results of this experiment show that if changes

of the oxidation-reduction potentials of soils are to be attributed to biological metabolism processes, experiments must be carried out under more standardized conditions, in order to eliminate such apparent causes of changes of potentials as pH and organic matter decomposition. The proper line of procedure undoubtedly lies in the analysis of all the different oxidation-reduction systems of the soil, and in the study of their relative concentrations.

Until more is known about the specific oxidation-reduction systems in soils, it seems that their importance, if any, must remain masked by the hydrogen and hydroxyl systems and the indefinite organic matter relationships. There seems to be a very promising field of investigation in the relationships of the latter system to changing potential, in view of the results shown by the soils of this experiment to which dried blood was added.

IV. SUMMARY.

1. The theory of oxidation-reduction potentials has been discussed in detail.
2. The methods of different investigators for determining the potentials of soils have been compared, and another method devised by the writer.
3. By means of a greenhouse study of four soils from different drainage conditions at different lime levels and different nitrogen fertilization, the relationships of the oxidation-reduction potentials of soils to nitrification, acidity, soil type, and fertilizer type was investigated.
4. It was found that any change of potential with nitrification is secondary to the effect of nitrification on pH.
5. The inverse relationship found by Herzner, Willis, and Heintze to exist between pH and E_h was verified.
6. Poorly drained and well drained soils, when dried to 3-25 per cent moisture, were found to have potentials of the same general magnitude.
7. The addition of $(NH_4)_2SO_4$ or $NaNO_3$ was found to have no effect on the potential.
8. The rapid decomposition of organic matter was found to cause a marked fall of potential.

V. APPENDIX

A. Tables

3. Moistures
4. Nitric nitrogen
5. Ammonic nitrogen
6. Acidity
7. Oxidation-reduction potentials

B. Charts 1 to 32

Graphic representation of the data of tables 4, 5, 6, and 7, arranged for the individual soils.

Table 3
Moisture content of soils

Date	Feb. 7	Feb. 23	March 10	March 20	April 4
Soil ^a	% moisture ^b	% moisture	% moisture	% moisture	% moisture
100	13.39	8.56	9.16	5.67	21.82
101	12.85	7.76	9.58	5.62	20.21
102	19.40	10.07	6.36	4.80	15.26
103	15.28	10.93	7.52	4.42	13.34
110	15.75	11.36	7.23	4.13	15.22
111	18.54	12.61	8.67	6.01	14.45
112	17.19	11.08	6.21	4.24	13.97
113	18.07	12.04	8.93	8.67	15.75
200	18.09	10.54	8.32	9.32	21.83
201	12.29	11.26	9.64	9.83	19.52
202	15.28	11.97	10.70	10.62	19.71
203	18.20	12.22	8.98	10.22	18.78
210	17.86	13.26	10.05	11.11	19.67
211	16.98	15.04	10.48	12.37	20.28
212	19.15	14.77	10.86	13.37	19.93
213	16.52	10.72	7.58	10.60	18.52
Date	Feb. 15	Feb. 23	March 16	March 23	April 10
Soil ^a	% moisture	% moisture	% moisture	% moisture	% moisture
300	22.16	13.44	6.48	3.13	14.64
301	21.79	14.24	7.24	6.78	16.18
302	22.98	11.92	7.18	3.49	12.82
303	24.02	9.79	6.89	4.29	13.59
310	24.33	11.56	8.51	5.10	14.40
311	24.76	11.08	7.71	5.70	17.78
312	22.77	13.33	5.52	3.45	18.56
313	23.24	12.11	9.65	4.05	16.13
400	26.63	21.30	10.04	8.43	22.92
401	26.53	17.60	13.34	7.72	21.26
402	25.12	17.85	9.66	8.00	22.00
403	26.55	16.94	9.39	7.81	19.48
410	25.63	17.77	14.32	13.21	23.56
411	25.53	21.48	12.60	9.55	23.61
412	25.21	23.02	15.31	11.31	22.92
413	25.22	19.27	12.58	12.30	24.28

a - See table 1 for treatment of soils.

b - All moisture determinations were calculated as percentages of moisture in moist soil.

Table 4

Concentrations of nitric nitrogen in soils

Date	Feb. 7	Feb. 23	March 10	March 20	April 4
Soil ^a	p.p.m. NO ₃ -N ^b	p.p.m. NO ₃ -N	p.p.m. NO ₃ -N	p.p.m. NO ₃ -N	p.p.m. NO ₃ -N
100	15	23	52	67	62
101	15	16	34	26	103
102	66	62	106	111	182
103	300	163	444	361	487
110	17	47	71	44	89
111	16	220	353	313	370
112	13	177	236	390	589
113	275	483	487	265	470
200	48	79	80	85	82
201	32	32	69	20	88
202	43	82	208	246	285
203	278	353	462	306	461
210	46	51	164	113	175
211	26	193	523	288	382
212	47	186	551	471	881
213	321	326	259	382	500
Date	Feb. 15	Feb. 28	March 16	March 28	April 10
Soil ^a	p.p.m. NO ₃ -N ^b	p.p.m. NO ₃ -N	p.p.m. NO ₃ -N	p.p.m. NO ₃ -N	p.p.m. NO ₃ -N
300	10	14	23	36	49
301	10	15	23	41	63
302	10	27	68	122	172
303	360	228	324	315	324
310	10	27	116	135	201
311	9	20	192	263	520
312	10	23	61	52	240
313	312	282	340	471	545
400	6	5	14	22	73
401	3	tr	tr	tr	tr
402	3	12	15	11	53
403	313	294	316	396	358
410	3	20	97	129	108
411	3	19	148	271	141
412	4	42	595	321	807
413	307	220	385	554	328

a - See table 1 for treatment of soils.

b - All determinations calculated on the basis of moisture-free soil.

Table 5

Concentrations of ammoniac nitrogen in soils

Date	Feb. 7	Feb. 23	March 10	March 20	April 4
Soil ^a	p.p.m. NH ₃ -N ^b	p.p.m. NH ₃ -N	p.p.m. NH ₃ -N	p.p.m. NH ₃ -N	p.p.m. NH ₃ -N
100	38	30	24	14	4
101	344	340	292	308	90
102	72	431	432	418	556
103	37	38	50	52	46
110	36	30	17	29	7
111	283	47	23	72	37
112	61	377	307	195	207
113	31	44	38	5	7
200	31	49	51	43	33
201	326	310	406	331	369
202	60		288	417	484
203	31	56	67	63	74
210	31	47	23	6	3
211	298	79	47	9	3
212	58	351	121	22	43
213	30	70	40	31	28
Date	Feb. 15	Feb. 28	March 16	March 28	April 10
Soil ^a	p.p.m. NH ₃ -N	p.p.m. NH ₃ -N	p.p.m. NH ₃ -N	p.p.m. NH ₃ -N	p.p.m. NH ₃ -N
300	14	75	7	8	6
301	334	340	236	194	247
302	55	425	432	357	444
303	18	66	32	27	37
310	21	72	20	23	5
311	321	235	135	78	40
312	70	463	349	325	363
313	21	105	66	56	41
400	34	82	64	64	36
401	258	283	360	379	477
402	82	595	686	689	783
403	31	79	87	96	114
410	46	85	31	10	28
411	333	357	161	111	76
412	98	552	157	178	9
413	41	87	58	21	10

a - See table 1 for soil treatments.

b - All determinations calculated on the basis of moisture-free soil.

Acidity of soils

Date	Feb. 11	Feb. 27	March 11	March 20	April 6
Soil ^a	pH	pH	pH	pH	pH
100	5.47	5.38	5.21	4.90	5.19
101	5.46	5.31	5.21	4.83	4.89
102	5.88	5.79	5.64	5.44	5.40
103	5.43	5.38	5.17	5.01	5.14
110	7.31	7.26	6.47	6.56	5.98
111	7.74	7.10	6.73	6.97	6.09
112	7.84	7.70	7.32	7.11	6.61
113	7.62	7.65	7.46	7.44	7.38
200	5.48	5.36	5.36	5.07	5.25
201	5.42	5.35	5.34	4.98	5.05
202	5.87	5.95	5.29	5.02	5.19
203	5.43	5.33	5.22	5.01	5.14
210	7.30	7.55	6.93	7.24	7.24
211	7.48	7.31	6.90	7.03	7.31
212	7.91	7.50	7.05	7.03	6.98
213	7.64	7.75	7.53	7.62	7.65
Date	Feb. 15	March 2	March 16	March 28	April 10
Soil ^a	pH	pH	pH	pH	pH
300	5.28	5.04	4.65	4.47	4.85
301	5.11	4.89	4.51	4.27	4.60
302	5.32	5.47	5.80	4.98	5.00
303	5.06	4.87	4.63	4.49	4.84
310	8.07	7.46	6.87	6.70	7.00
311	8.16	7.74	7.23	6.90	6.80
312	8.17	8.07	7.42	7.35	7.52
313	8.09	7.80	7.55	7.03	7.54
400	5.15	5.30	4.82	4.74	5.02
401	5.16	4.98	4.71	4.68	5.00
402	5.39	5.52	5.50	5.42	5.49
403	5.16	4.95	4.81	4.70	5.00
410	7.01	6.47	6.00	6.18	6.08
411	7.64	6.91	6.55	6.15	6.21
412	7.68	7.33	6.53	6.32	6.10
413	7.64	7.05	7.06	6.67	6.71

a - See table 1 for soil treatments.

Table 7
Oxidation-reduction potentials^b of soils

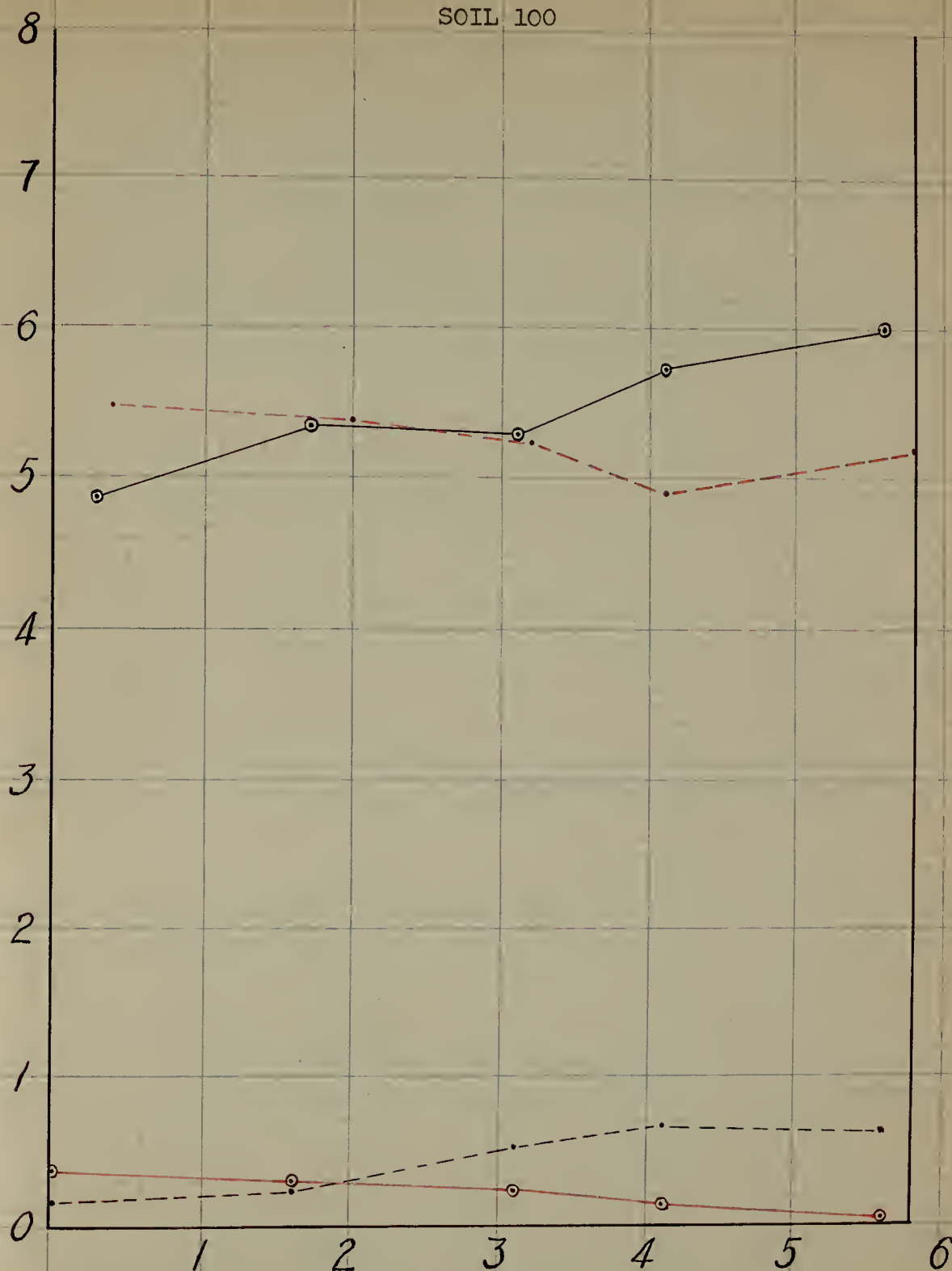
Date	Feb. 10	Feb. 24	March 10	March 20	April 4
Soil ^a	E _h (volt)	E _h (volt)	E _h (volt)	E _h (volt)	E _h (volt)
100	+ .488	+ .532	+ .529	+ .571	+ .600
101	+ .493	+ .532	+ .530	+ .603	+ .615
102	+ .486	+ .488	+ .500	+ .452	+ .499
103	+ .484	+ .571	+ .544	+ .563	+ .585
110	+ .386	+ .435	+ .448	+ .434	+ .486
111	+ .386	+ .431	+ .447	+ .441	+ .485
112	+ .040	+ .313	+ .365	+ .419	+ .467
113	+ .387	+ .433	+ .441	+ .442	+ .487
200	+ .479	+ .560	+ .558	+ .576	+ .575
201	+ .479	+ .561	+ .556	+ .599	+ .589
202	+ .462	+ .494	+ .556	+ .569	+ .583
203	+ .477	+ .560	+ .563	+ .582	+ .583
210	+ .357	+ .448	+ .463	+ .466	+ .473
211	+ .362	+ .454	+ .474	+ .439	+ .501
212	+ .085	+ .368	+ .450	+ .430	+ .507
213	+ .356	+ .442	+ .449	+ .481	+ .487
Date	Feb. 16	March 1	March 16	March 28	April 10
Soil ^a	E _h (volt)	E _h (volt)	E _h (volt)	E _h (volt)	E _h (volt)
300	+ .523	+ .558	+ .553	+ .561	+ .614
301	+ .524	+ .575	+ .575	+ .597	+ .617
302	+ .471	+ .093	+ .343	+ .457	+ .403
303	+ .560	+ .575	+ .568	+ .563	+ .533
310	+ .328	+ .389	+ .392	+ .435	+ .513
311	+ .321	+ .388	+ .374	+ .426	+ .503
312	+ .020	- .030	+ .030	+ .038	+ .377
313	+ .318	+ .400	+ .382	+ .415	+ .458
400	+ .491	+ .537	+ .540	+ .556	+ .590
401	+ .499	+ .544	+ .564	+ .535	+ .570
402	+ .391	+ .265	+ .306	+ .368	+ .477
403	+ .504	+ .535	+ .536	+ .543	+ .560
410	+ .378	+ .429	+ .447	+ .476	+ .496
411	+ .372	+ .440	+ .458	+ .460	+ .500
412	+ .103	+ .191	+ .355	+ .403	+ .517
413	+ .387	+ .413	+ .419	+ .479	+ .499

^a - See table 1 for soil treatments.

^b - Expressed as the potential of the half-cell, | soil suspension | Pt,
at 35°C.

Chart 1

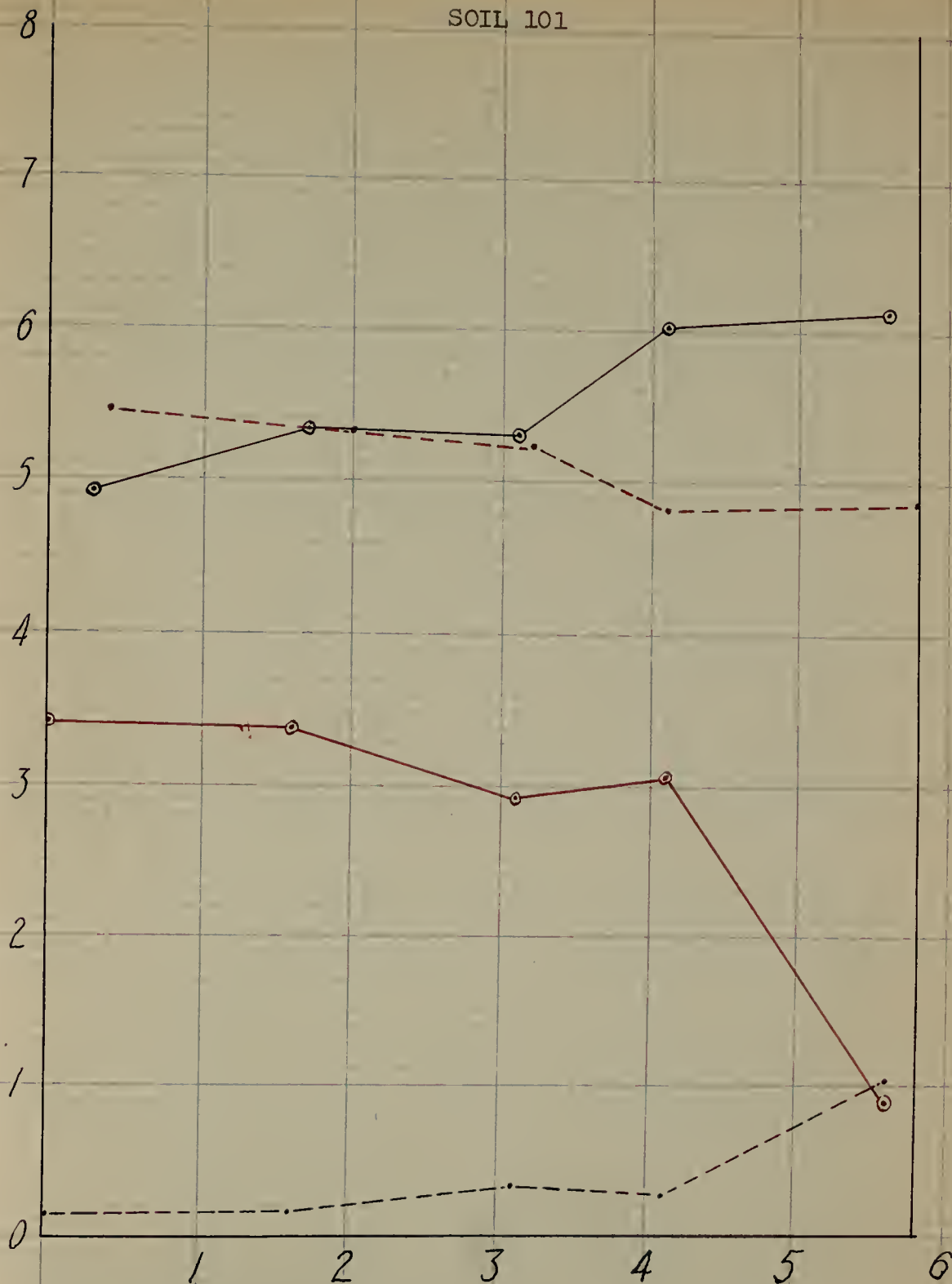
SOIL 100



ORDINATES - NO₃-N (·- - - ·); 1 large division = 100 p.p.m.
 NH₃-N (○- - - ○); 1 large division = 100 p.p.m.
 pH (·- - - ·); 1 large division = 1 pH.
 E_h (○- - - ○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 2
SOIL 101

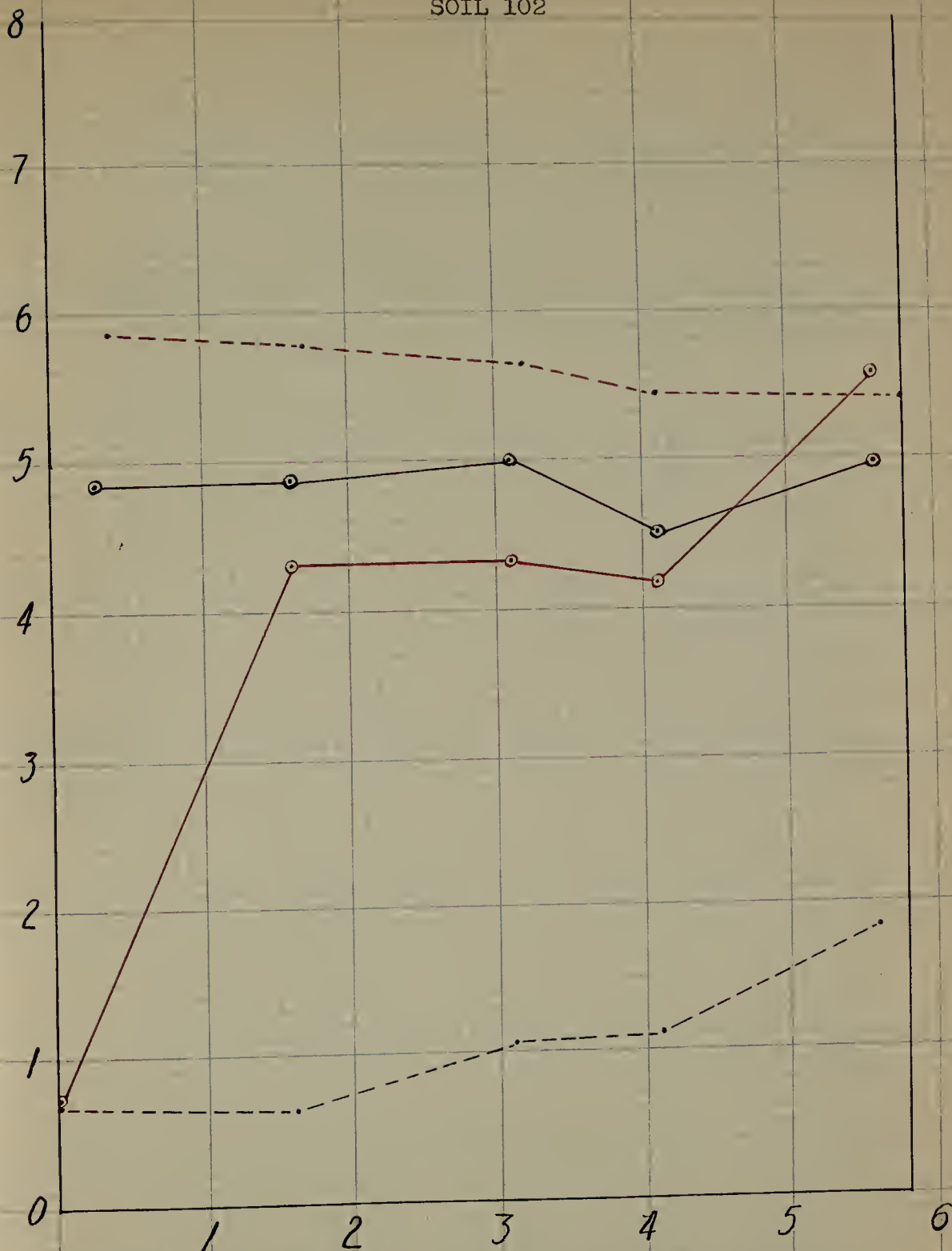


ORDINATES - NO₃-N (·-·-·); 1 large division = 100 p.p.m.
 NH₃-N (○-○); 1 large division = 100 p.p.m.
 pH (·-·-·); 1 large division = 1 pH.
 E_h (○-○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 3

SOIL 102

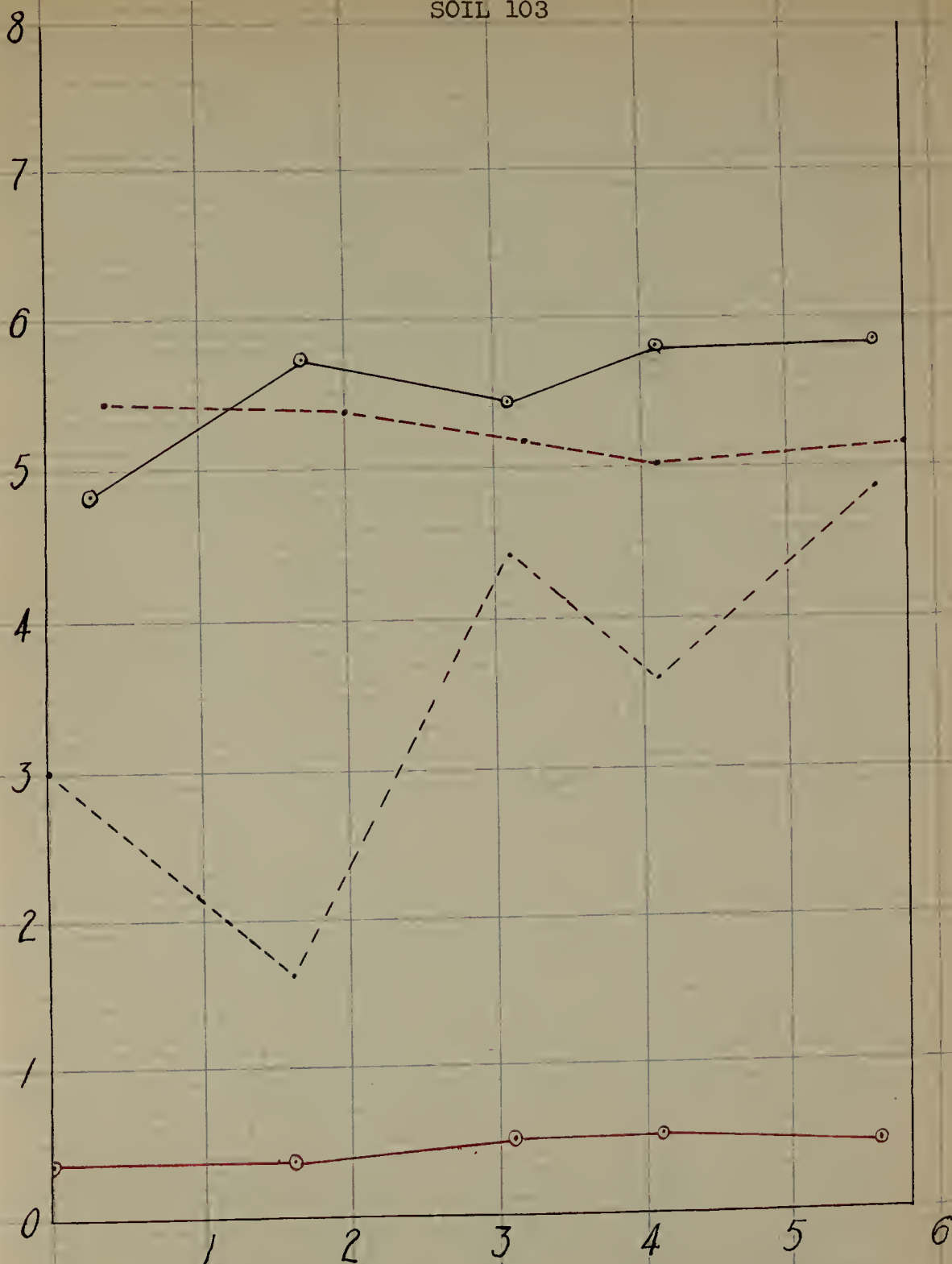


ORDINATES - NO₃-N (·- - -·); 1 large division = 100 p.p.m.
 NH₃-N (○- - -○); 1 large division = 100 p.p.m.
 pH (·- - -·); 1 large division = 1 pH.
 E_h (○- - -○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 4

SOIL 103

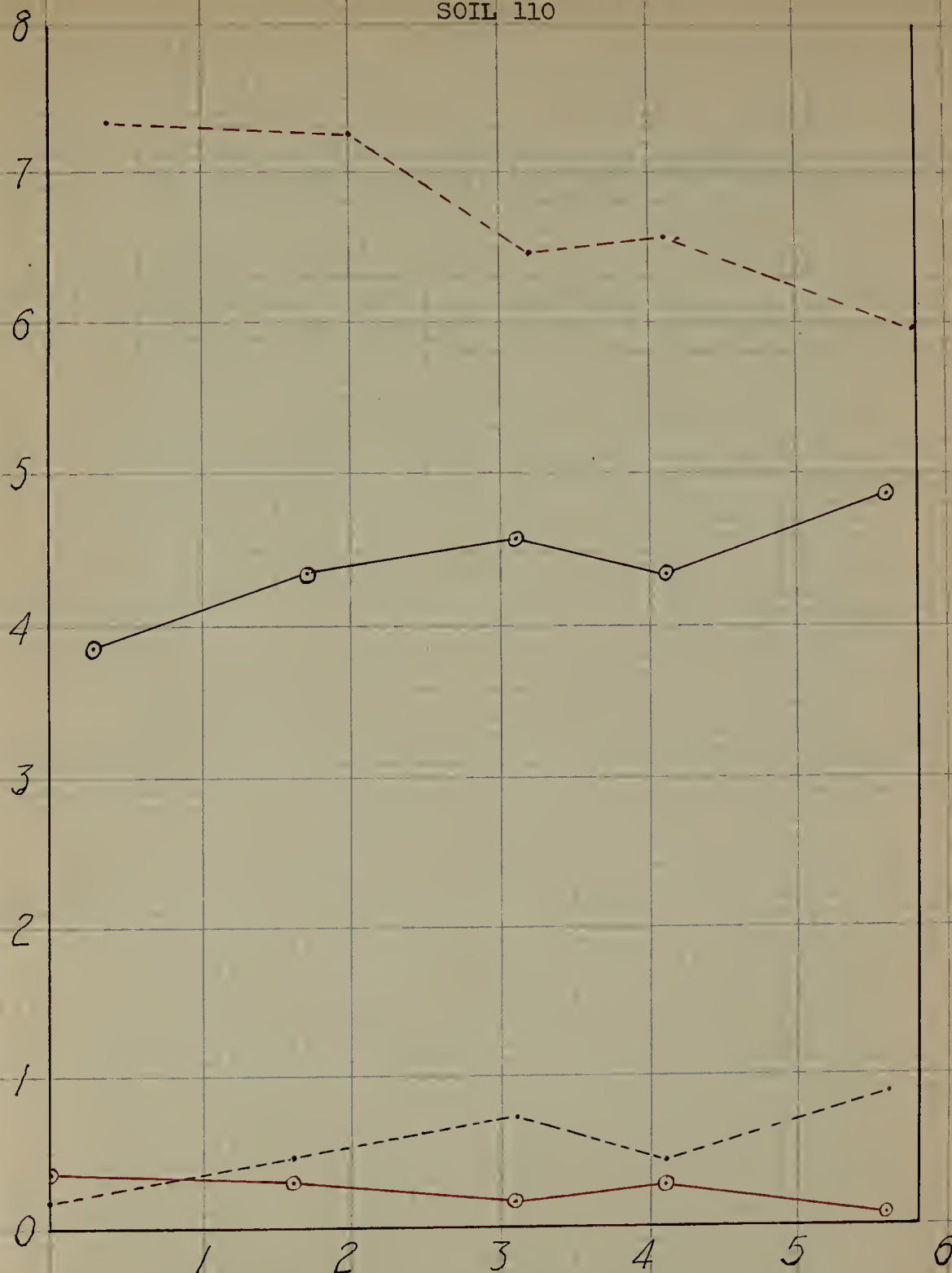


ORDINATES - NO₃-N (·-·-·-·); 1 large division = 100 p.p.m.
 NH₃-N (○-○-○); 1 large division = 100 p.p.m.
 pH (·-·-·-·); 1 large division = 1 pH.
 E_h (○-○-○); 1 large division = .1 volt

ABSCISSAS - Time; 1 large division = 10 days.

Chart 5

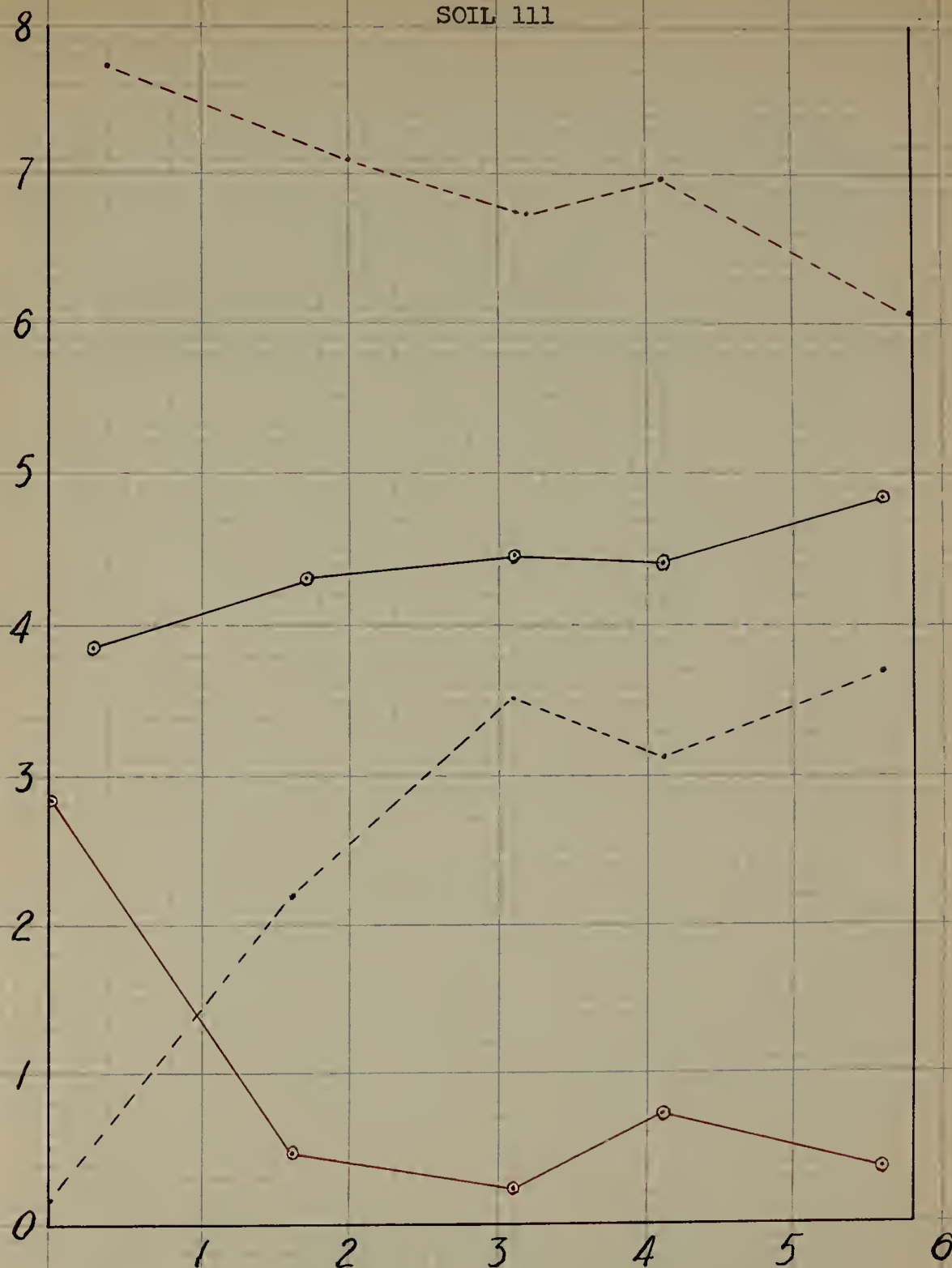
SOIL 110



ORDINATES - NO₃-N (----); 1 large division = 100 p.p.m.
 NH₃-N (○—○); 1 large division = 100 p.p.m.
 pH₃ (-.-.-); 1 large division = 1 pH.
 E_h (○—○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

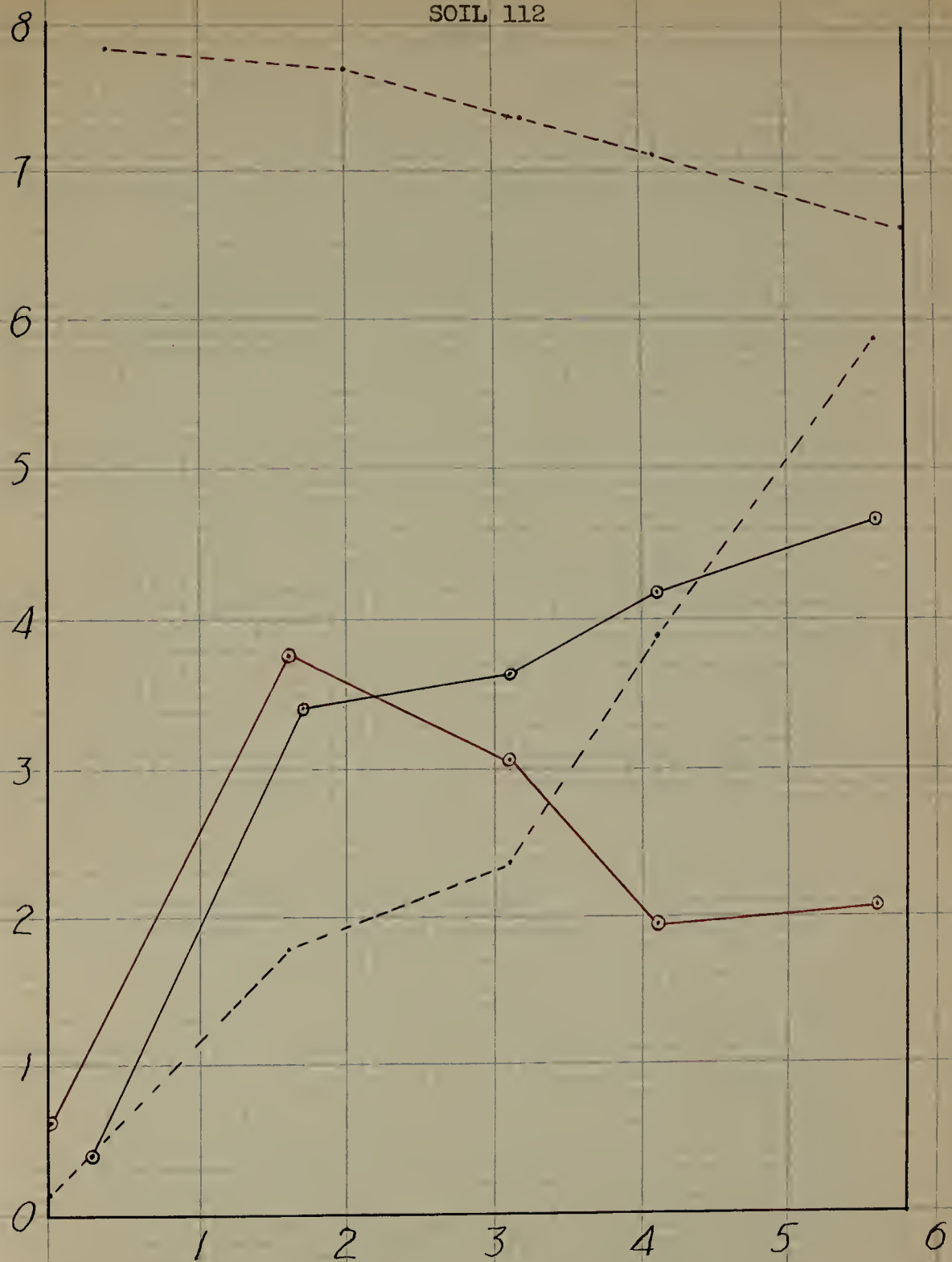
Chart 6
SOIL 111



ORDINATES - NO₃-N (·---·); 1 large division = 100 p.p.m.
 NH₃-N (⊙—⊙); 1 large division = 100 p.p.m.
 pH (·---·); 1 large division = 1 pH.
 E_h (⊙—⊙); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

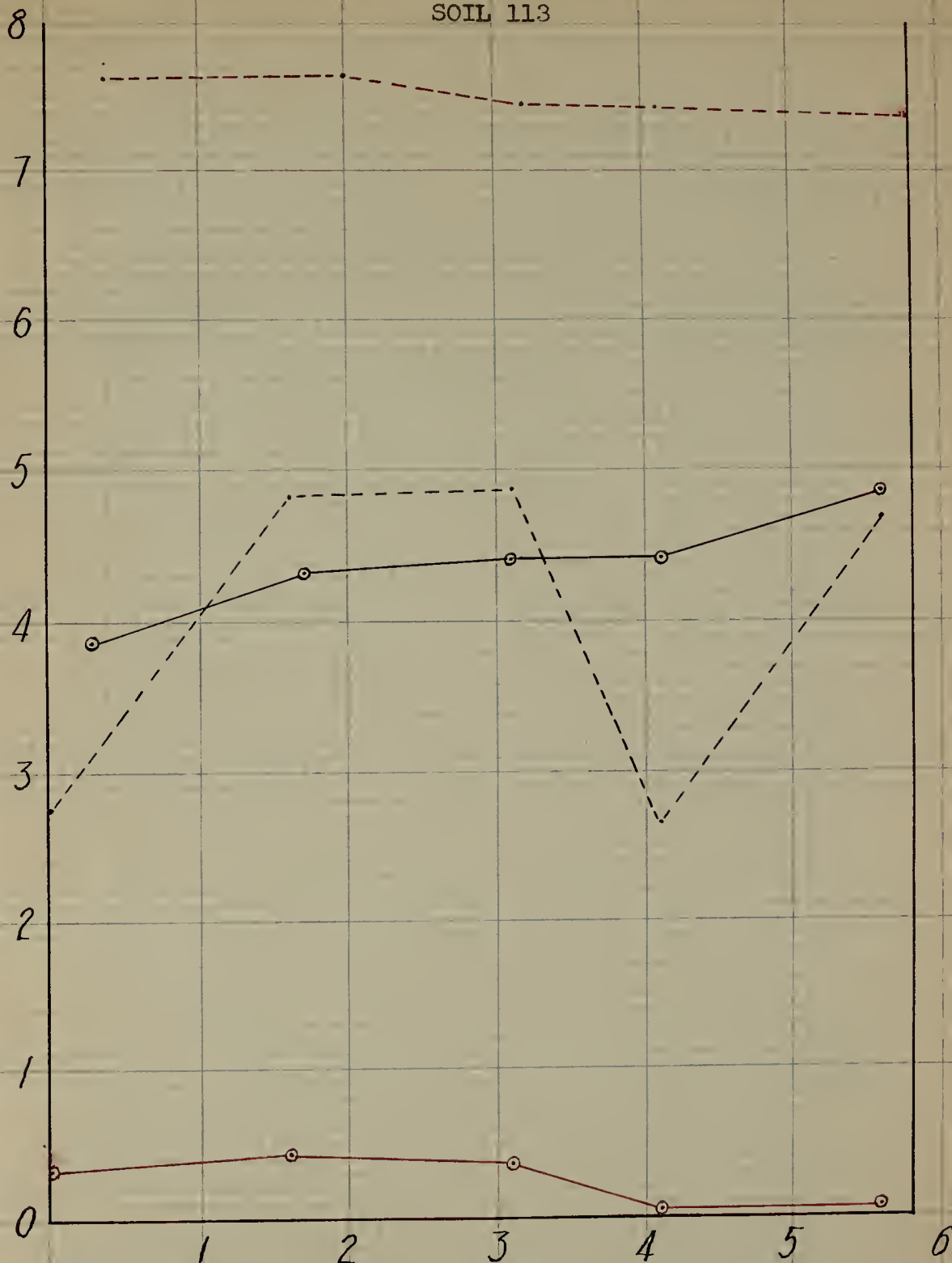
Chart 7
SOIL 112



ORDINATES - NO₃-N (·-·-·); 1 large division = 100 p.p.m.
NH₃-N (○-○); 1 large division = 100 p.p.m.
pH (·-·-·); 1 large division = 1 pH.
E_h (○-○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

SOIL 113

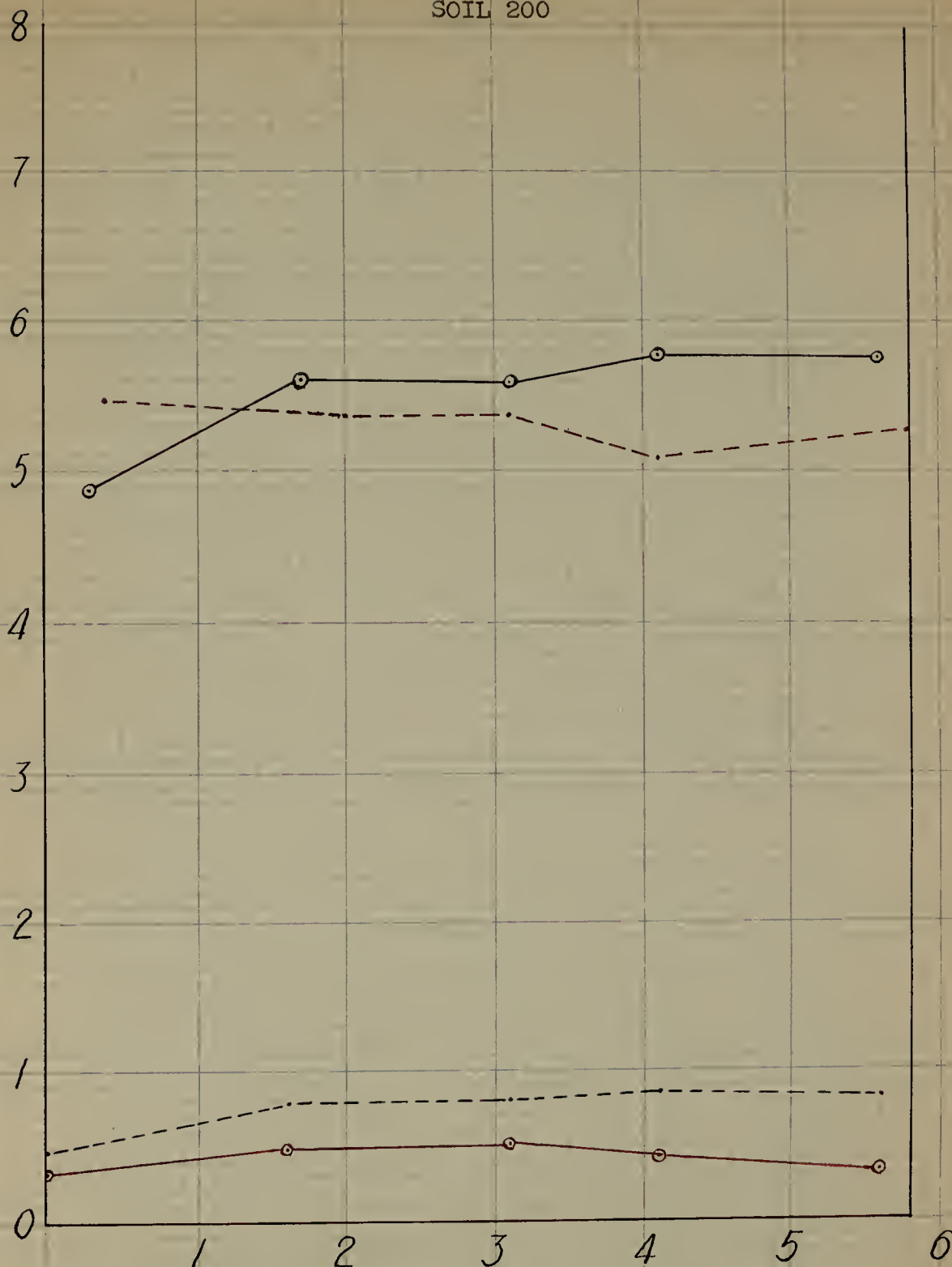


ORDINATES - NO₃-N (·-·-·-·); 1 large division = 100 p.p.m.
 NH₃-N (○-○-○); 1 large division = 100 p.p.m.
 pH (·-·-·-·); 1 large division = 1 pH.
 Eh (○-○-○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 9

SOIL 200

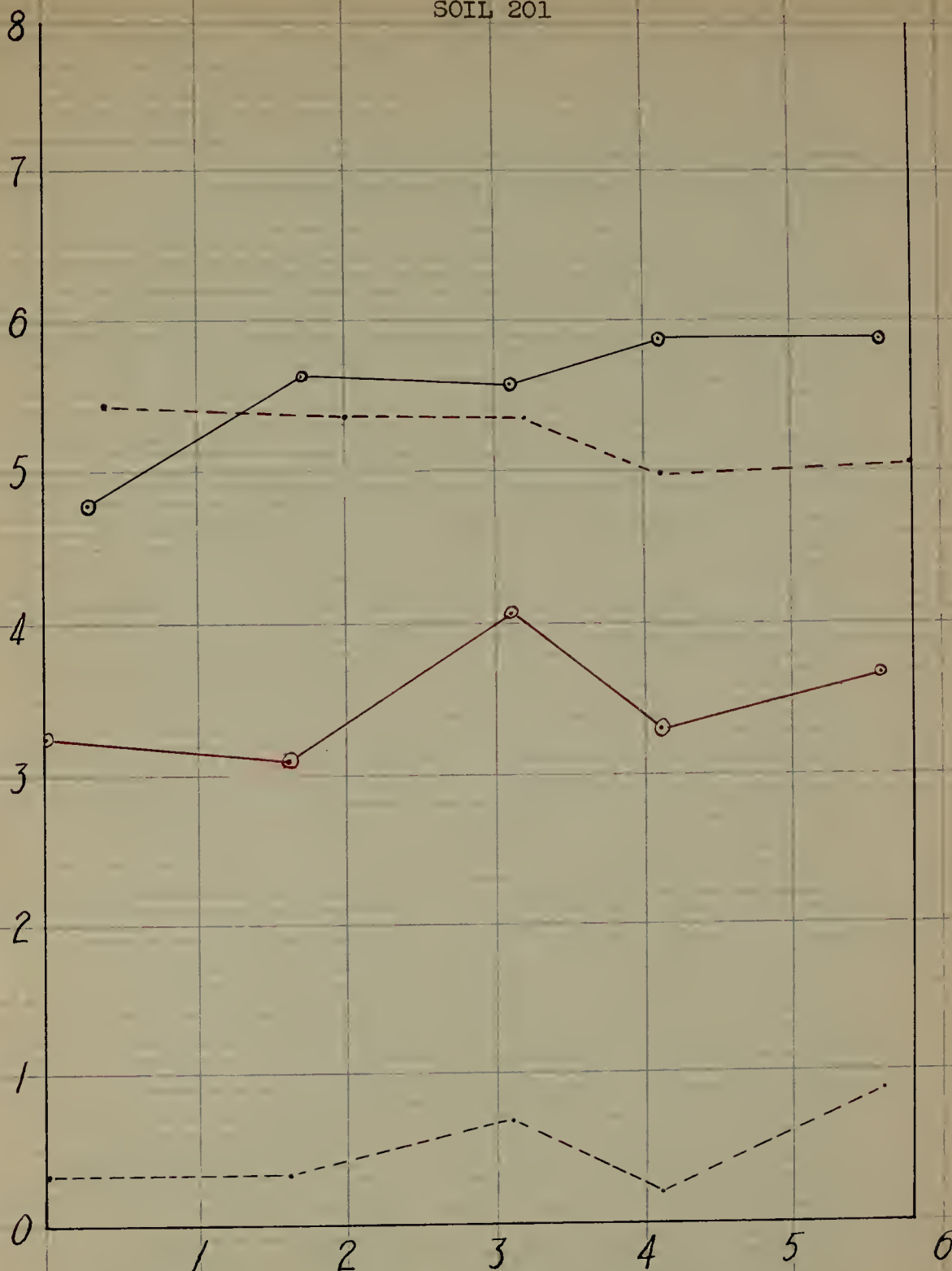


ORDINATES - NO₃-N (·---·); 1 large division = 100 p.p.m.
 NH₃-N (○—○); 1 large division = 100 p.p.m.
 pH (·---·); 1 large division = 1 pH.
 E_h (○—○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 10

SOIL 201

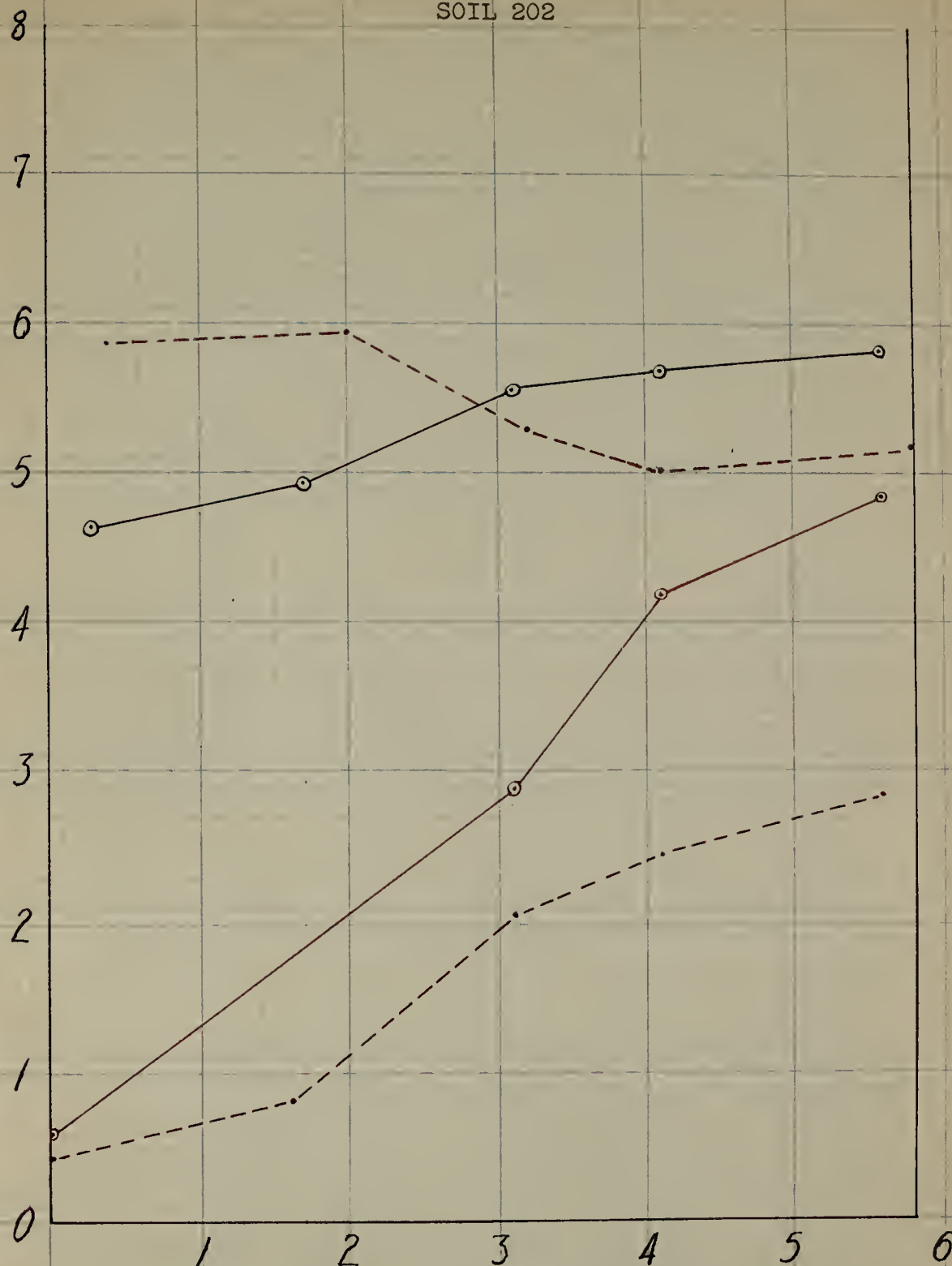


ORDINATES - NO₃-N (·-·-·); 1 large division = 100 p.p.m.
 NH₃-N (○-○); 1 large division = 100 p.p.m.
 pH (·-·-·); 1 large division = 1 pH.
 E_h (○-○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 11

SOIL 202

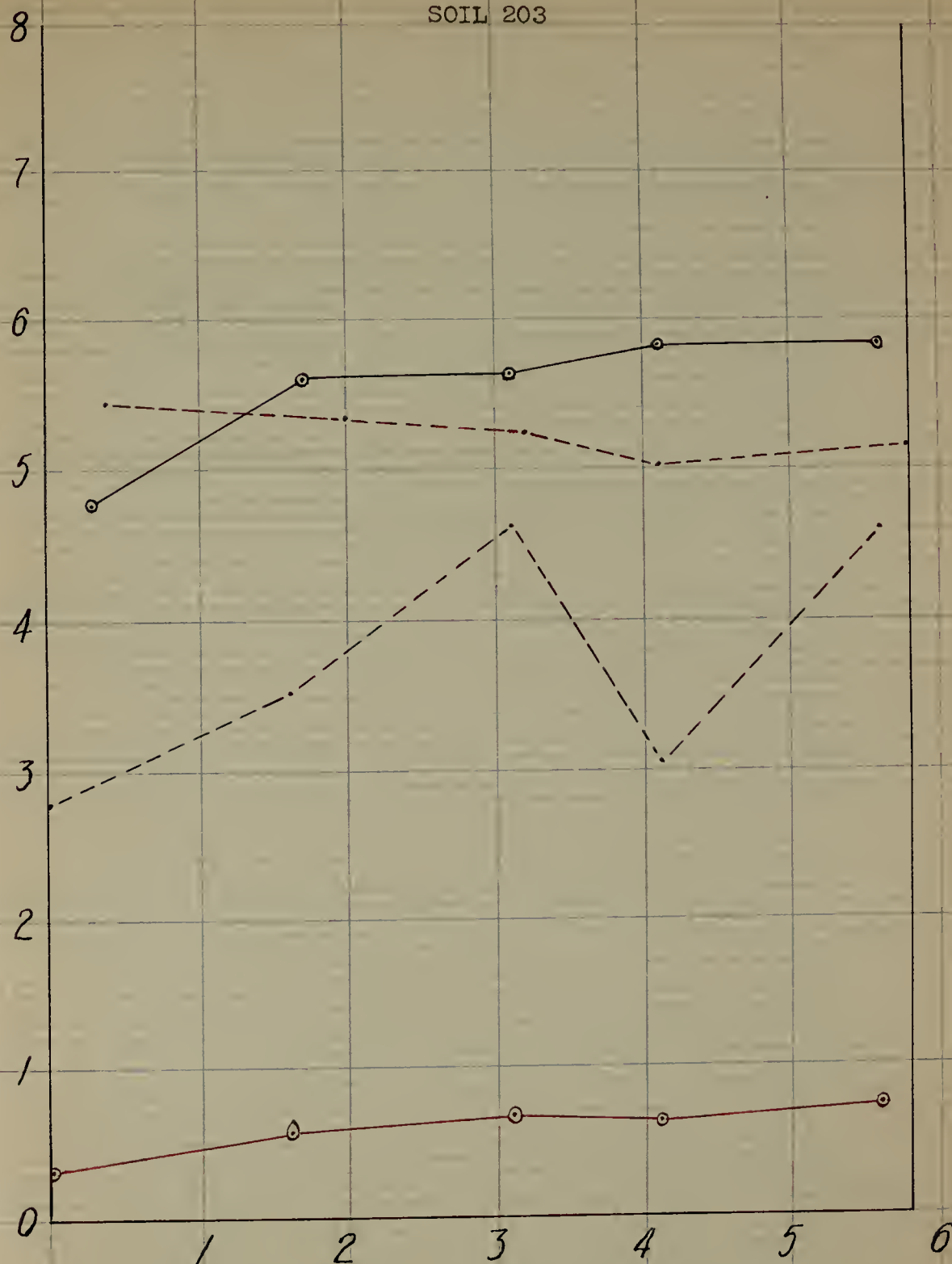


ORDINATES - NO₃-N (·-·-·-·); 1 large division = 100 p.p.m.
 NH₃-N (○-○-○); 1 large division = 100 p.p.m.
 pH (·-·-·-·); 1 large division = 1 pH.
 E_h (○-○-○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 12

SOIL 203

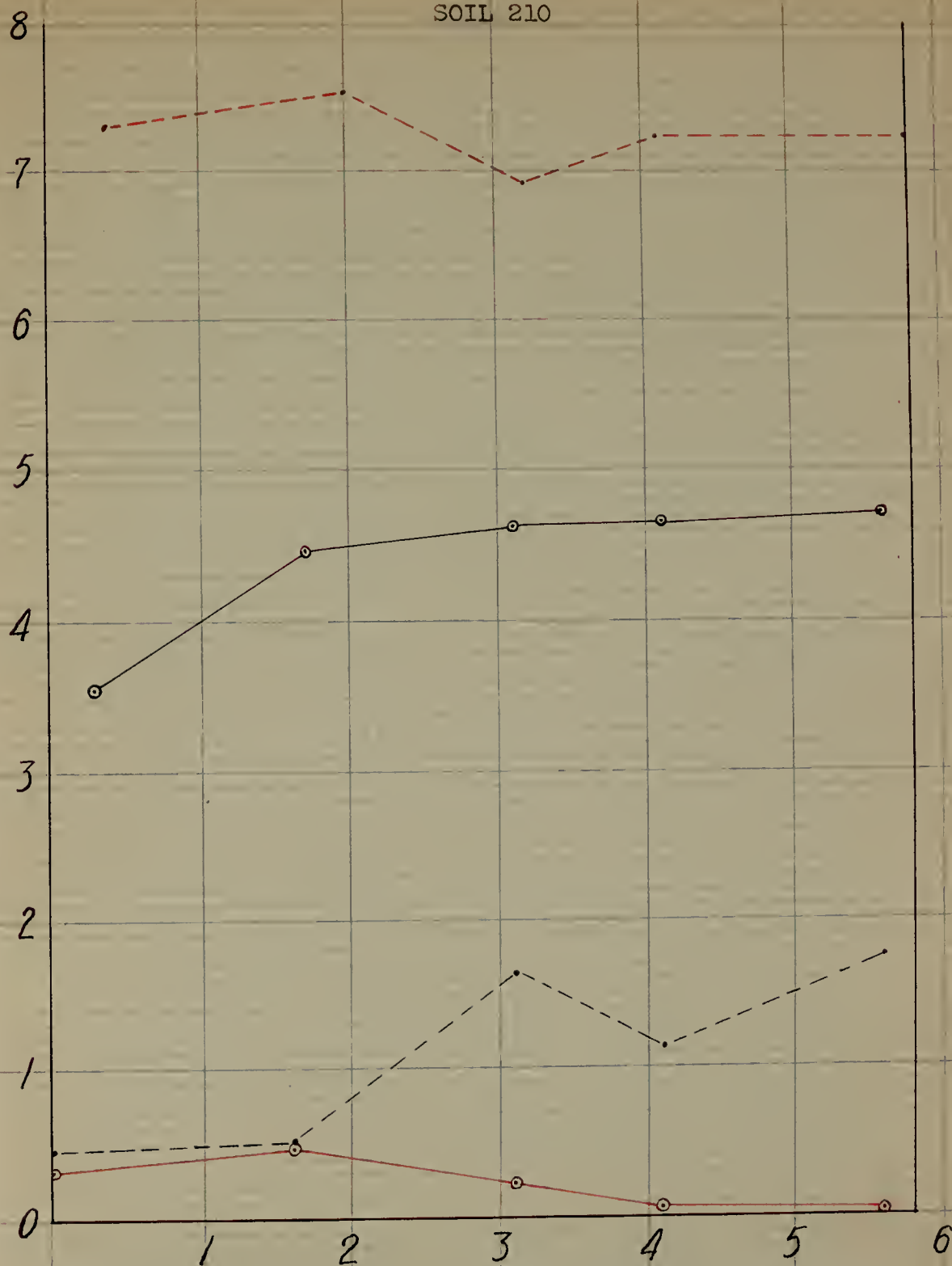


ORDINATES - NO₃-N (----); 1 large division = 100 p.p.m.
 NH₃-N (○—○); 1 large division = 100 p.p.m.
 pH (····); 1 large division = 1 pH.
 E_h (○—○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 13

SOIL 210

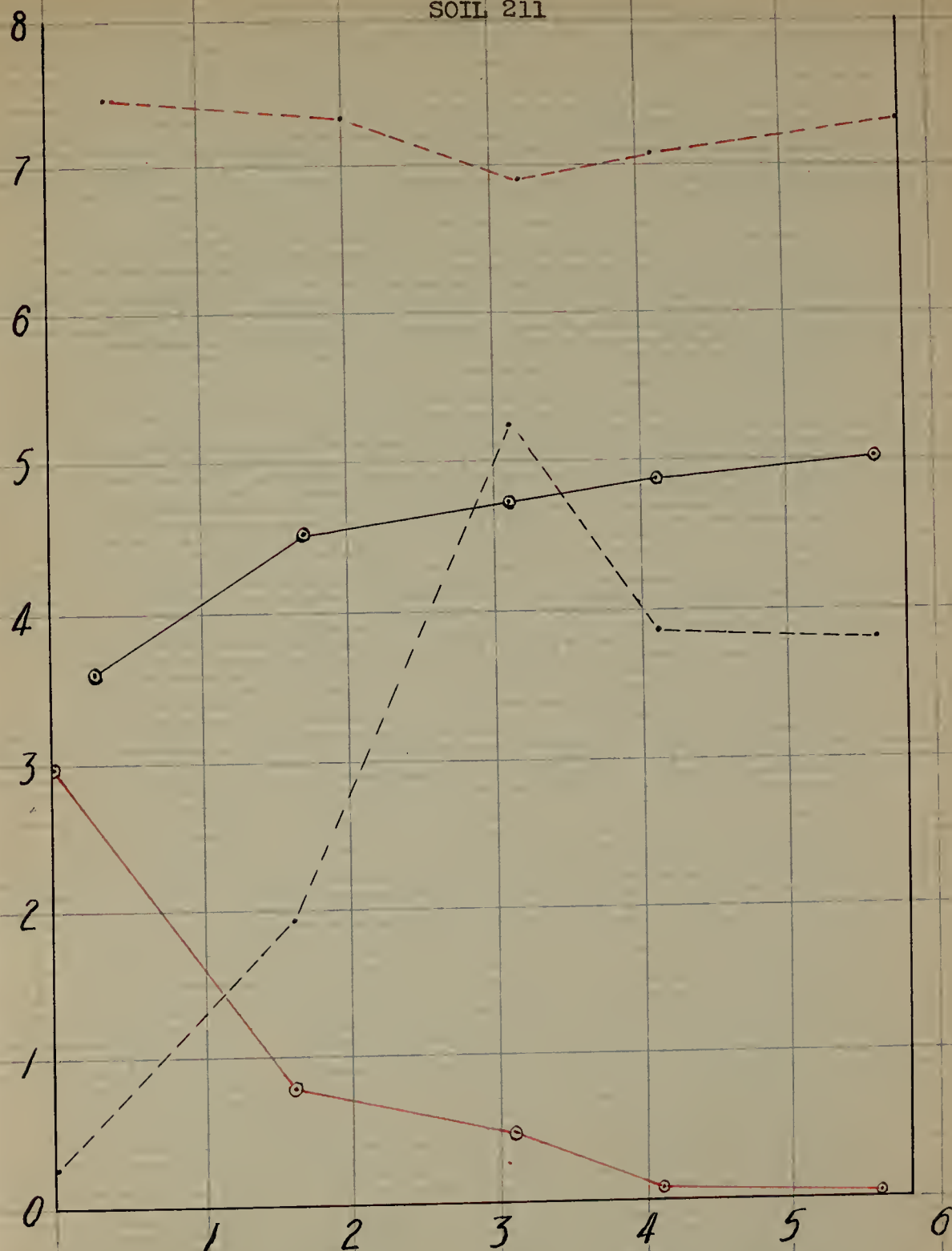


ORDINATES - NO₃-N (·---·); 1 large division = 100 p.p.m.
 NH₃-N (○—○); 1 large division = 100 p.p.m.
 pH (·---·); 1 large division = 1 pH.
 E_h (○—○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 14

SOIL 211

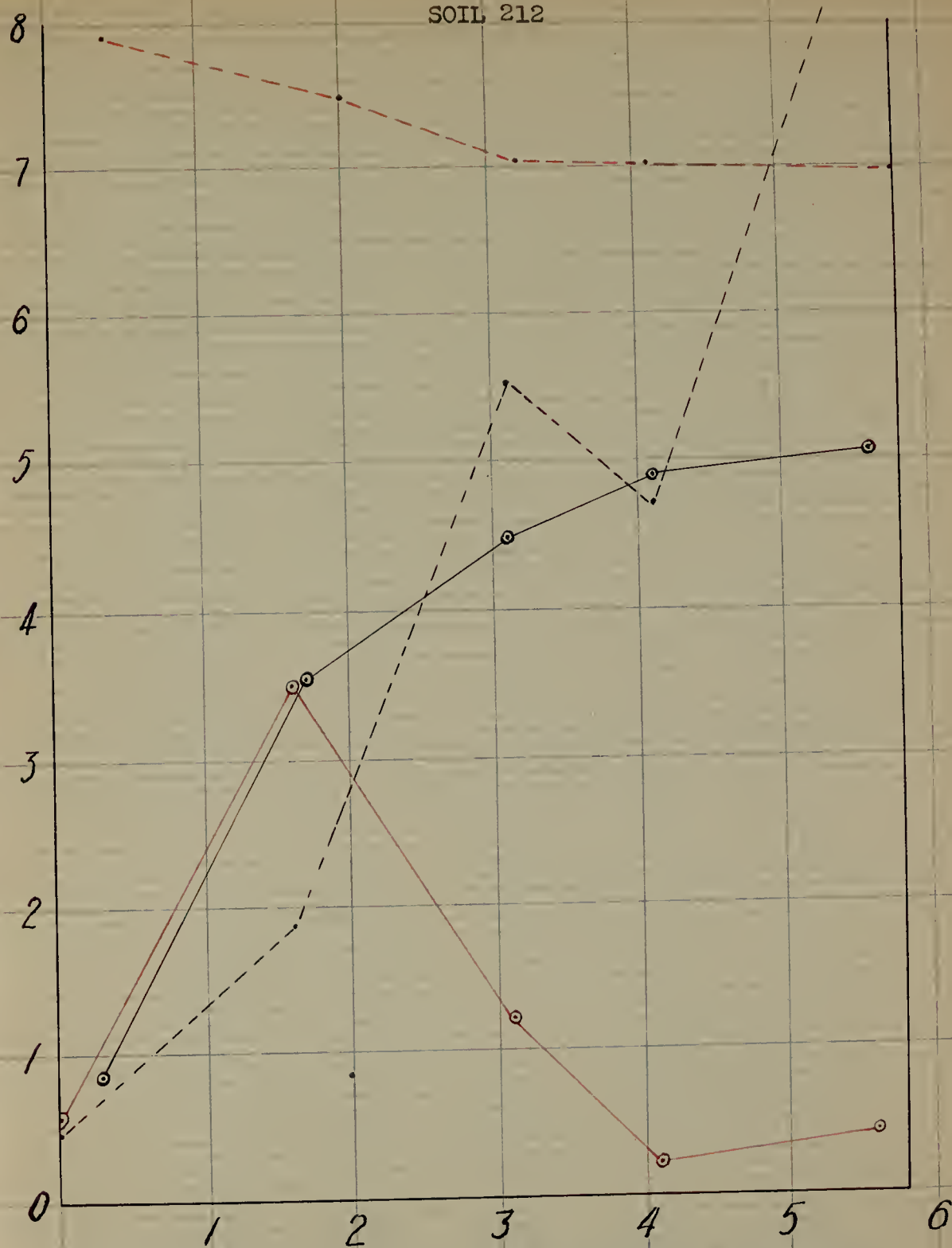


ORDINATES - NO₃-N (·---·); 1 large division = 100 p.p.m.
 NH₃-N (○—○); 1 large division = 100 p.p.m.
 pH (·---·); 1 large division = 1 pH.
 E_h (○—○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 15

SOIL 212

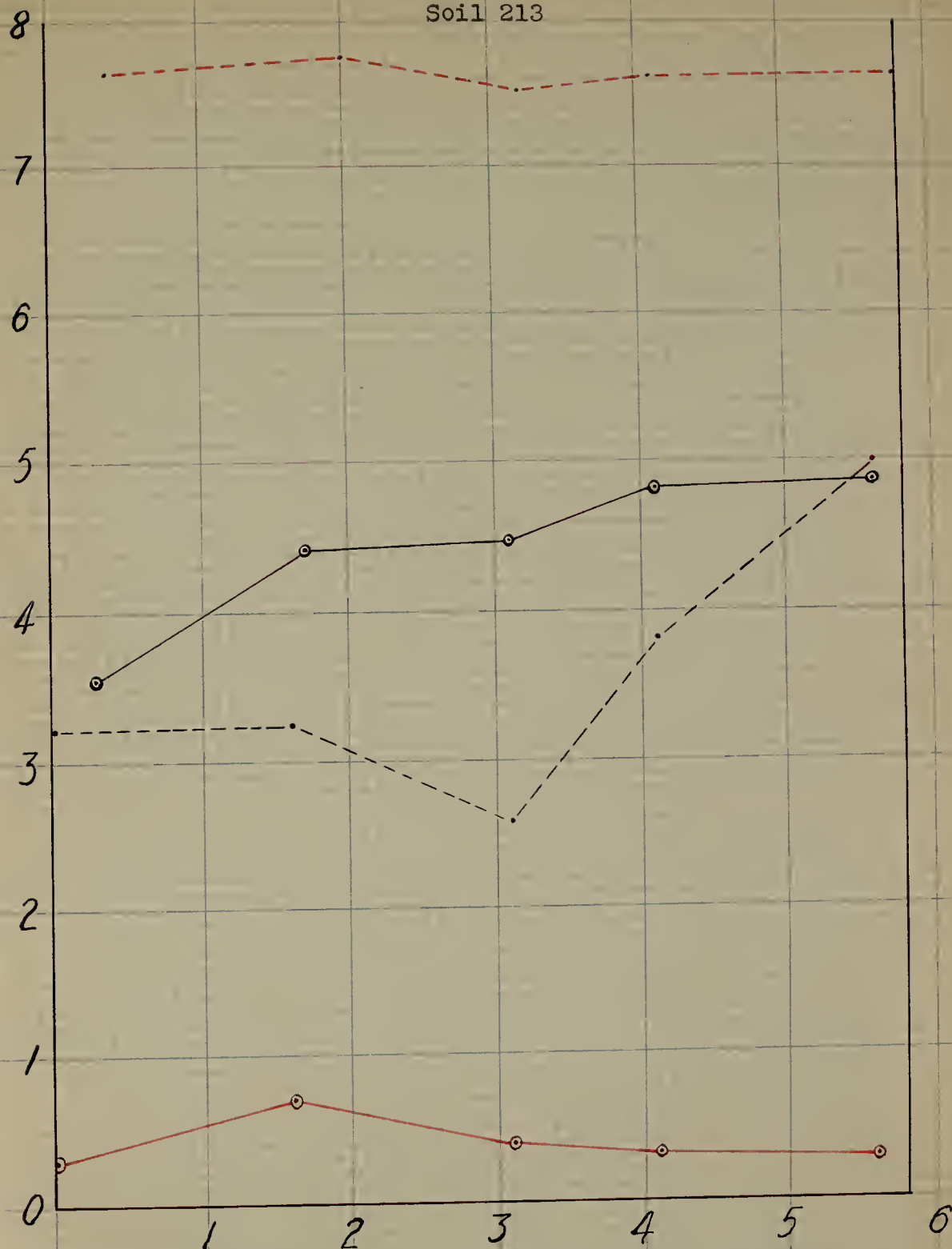


ORDINATES - NO₃-N (·---·); 1 large division = 100 p.p.m.
 NH₃-N (⊙—⊙); 1 large division = 100 p.p.m.
 pH (·---·); 1 large division = 1 pH.
 E_h (⊙—⊙); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 16

Soil 213

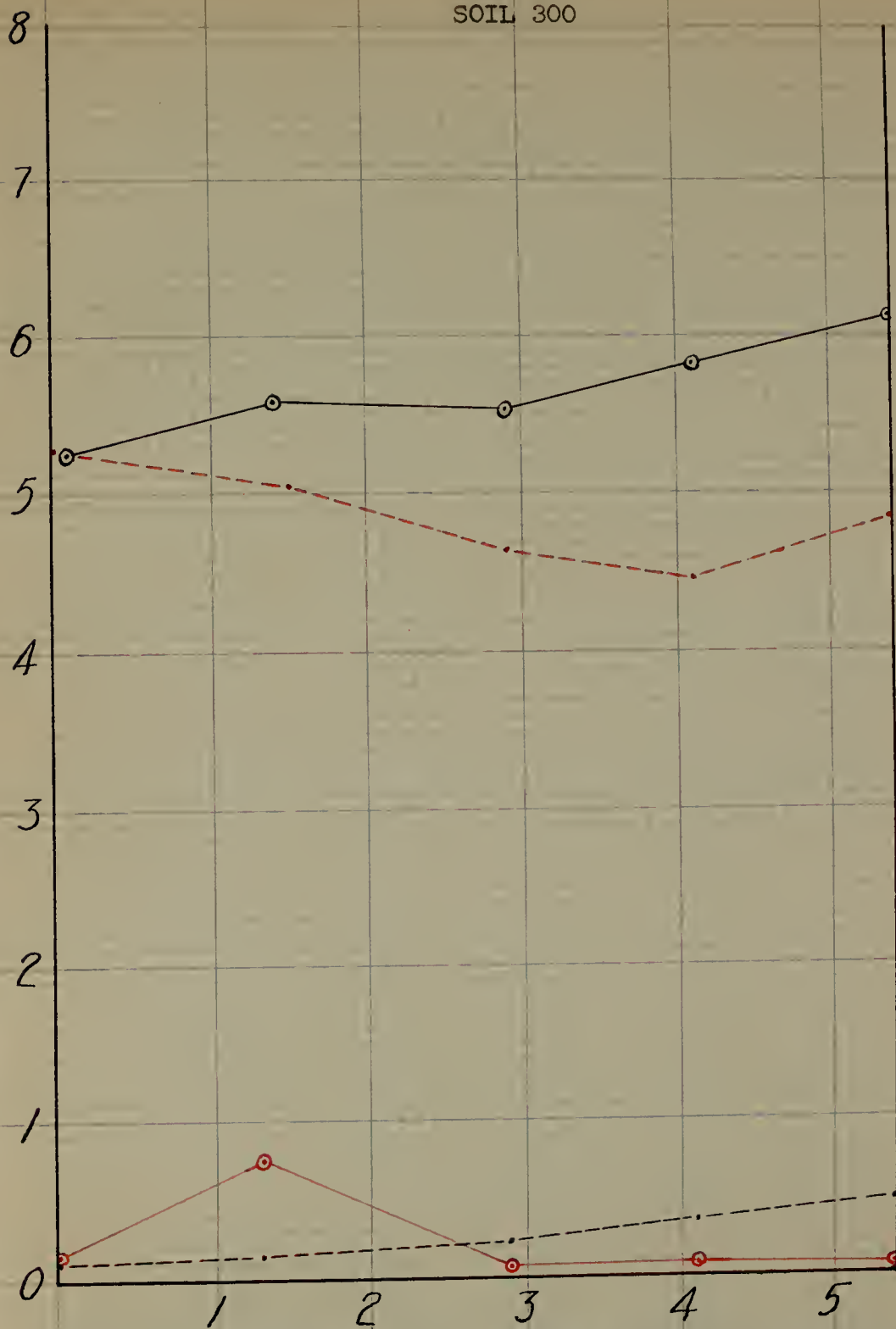


ORDINATES - NO₃-N (·- - - ·); 1 large division = 100 p.p.m.
 NH₃-N (○- - - ○); 1 large division = 100 p.p.m.
 pH (·- - - ·); 1 large division = 1 pH.
 E_h (○- - - ○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 17

SOIL 300

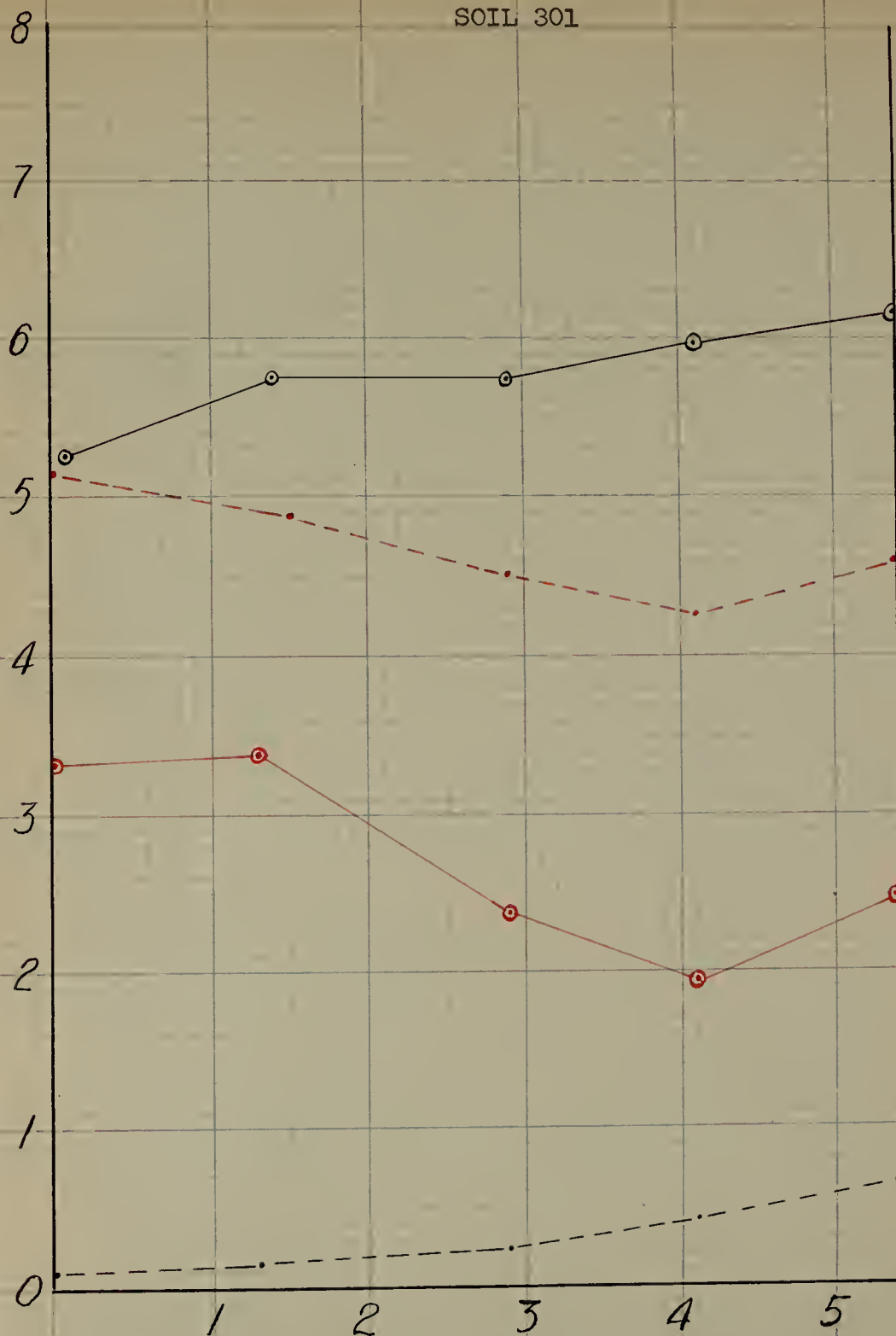


ORDINATES - NO₃-N (·---·); 1 large division = 100 p.p.m.
 NH₃-N (○—○); 1 large division = 100 p.p.m.
 pH (·---·); 1 large division = 1 pH.
 E_h (○—○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 18

SOIL 301

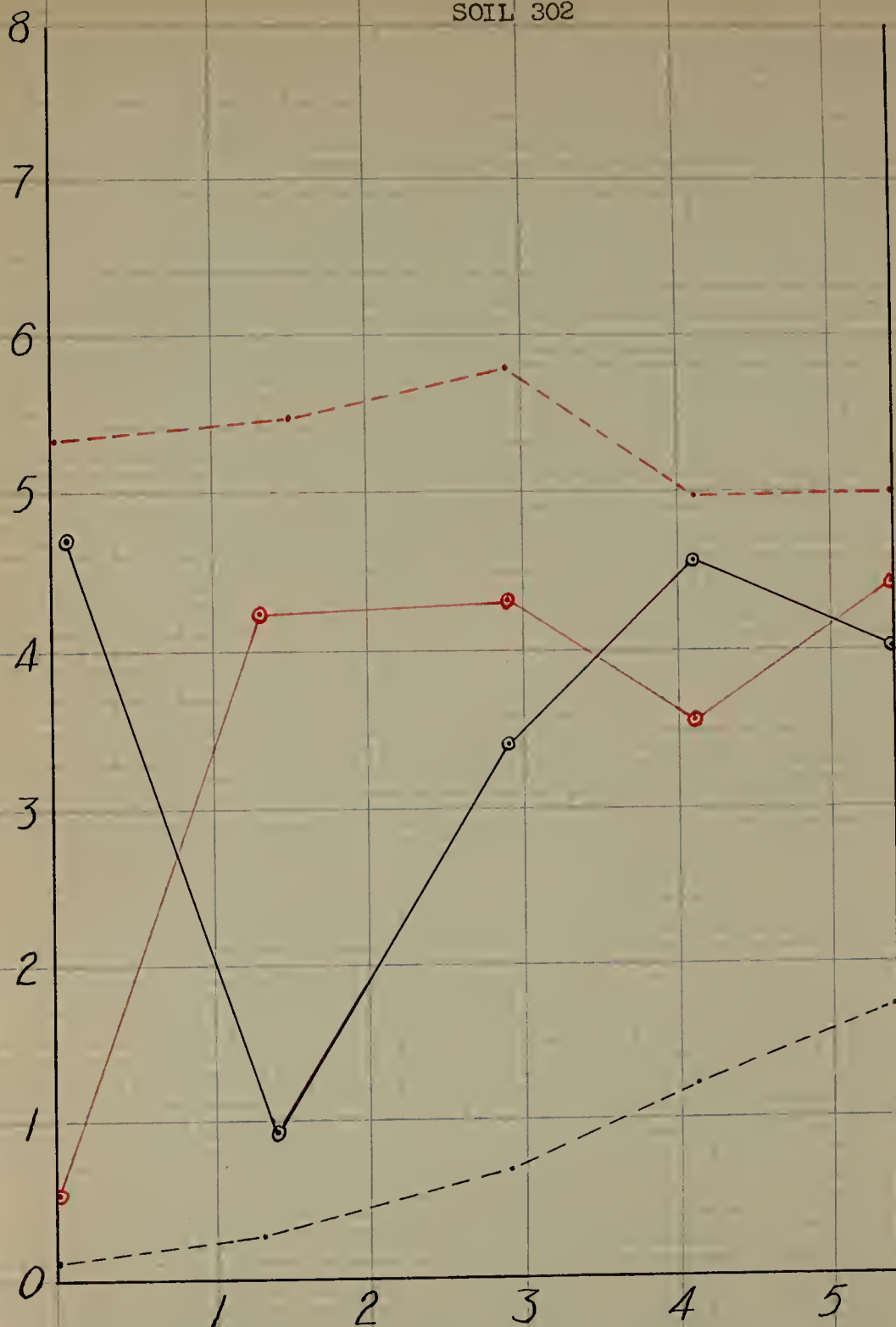


ORDINATES - NO₃-N (·- - -·); 1 large division = 100 p.p.m.
 NH₃-N (○—○); 1 large division = 100 p.p.m.
 pH (·- - -·); 1 large division = 1 pH.
 E_h (○—○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 19

SOIL 302

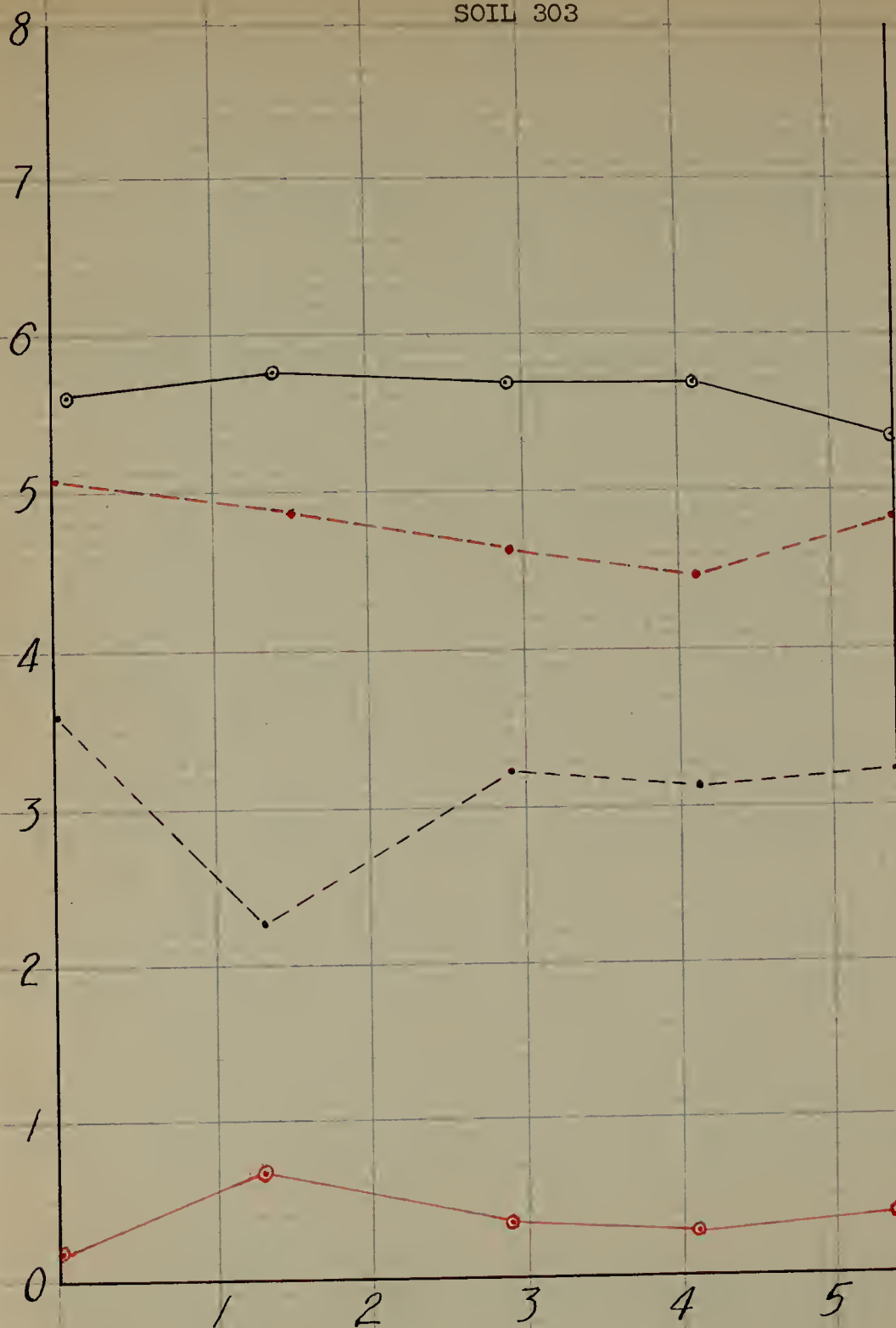


ORDINATES - NO₃-N (·---·); 1 large division = 100 p.p.m.
 NH₃-N (●---●); 1 large division = 100 p.p.m.
 pH (·---·); 1 large division = 1 pH.
 E_h (○---○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 20

SOIL 303

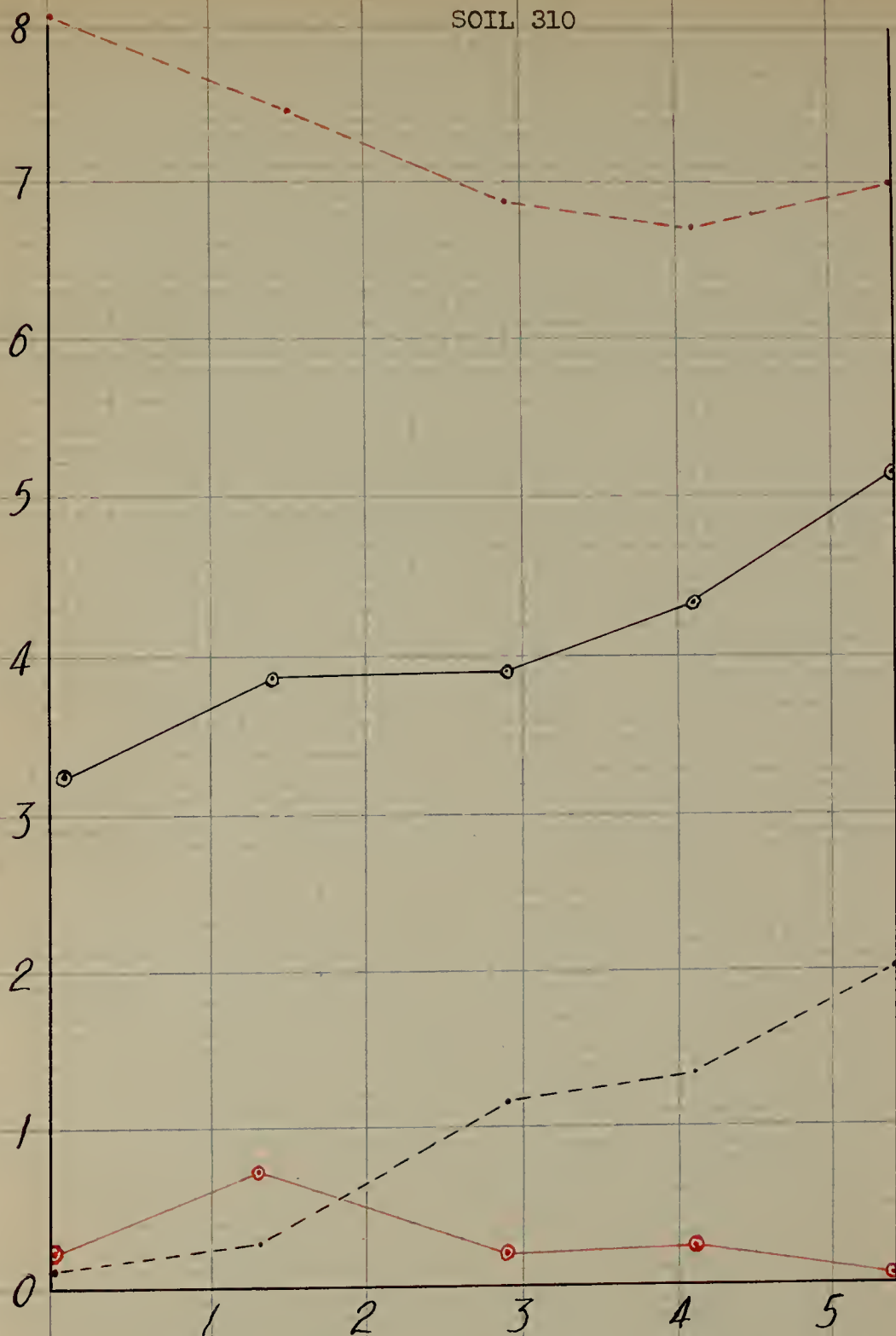


ORDINATES - NO₃-N (·---·); 1 large division = 100 p.p.m.
 NH₃-N (○—○); 1 large division = 100 p.p.m.
 pH (·---·); 1 large division = 1 pH.
 E_h (○—○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 21

SOIL 310

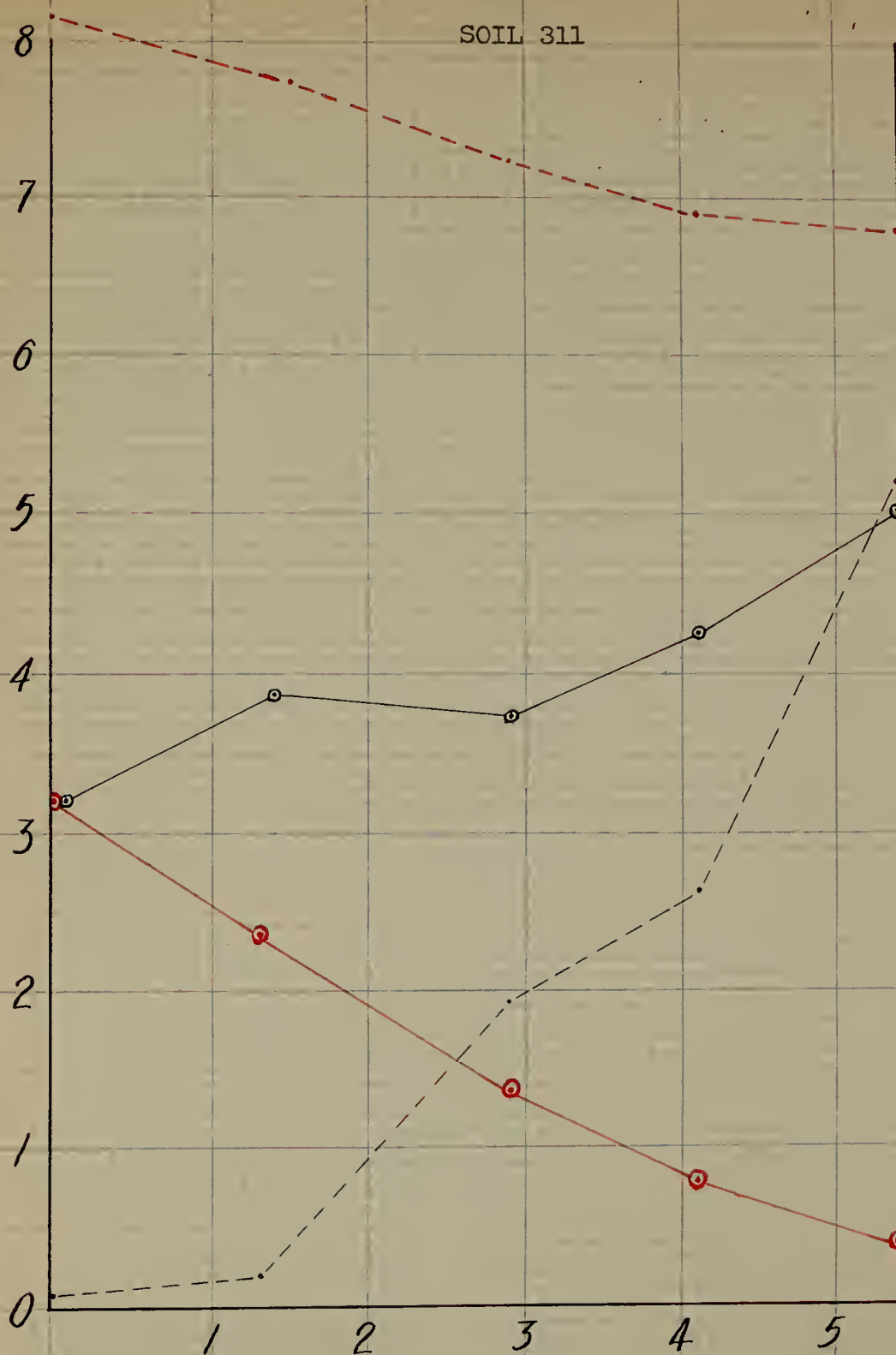


ORDINATES - NO₃-N (·---·); 1 large division = 100 p.p.m.
 NH₃-N (○—○); 1 large division = 100 p.p.m.
 pH (·---·); 1 large division = 1 pH.
 E_h (○—○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 22

SOIL 311

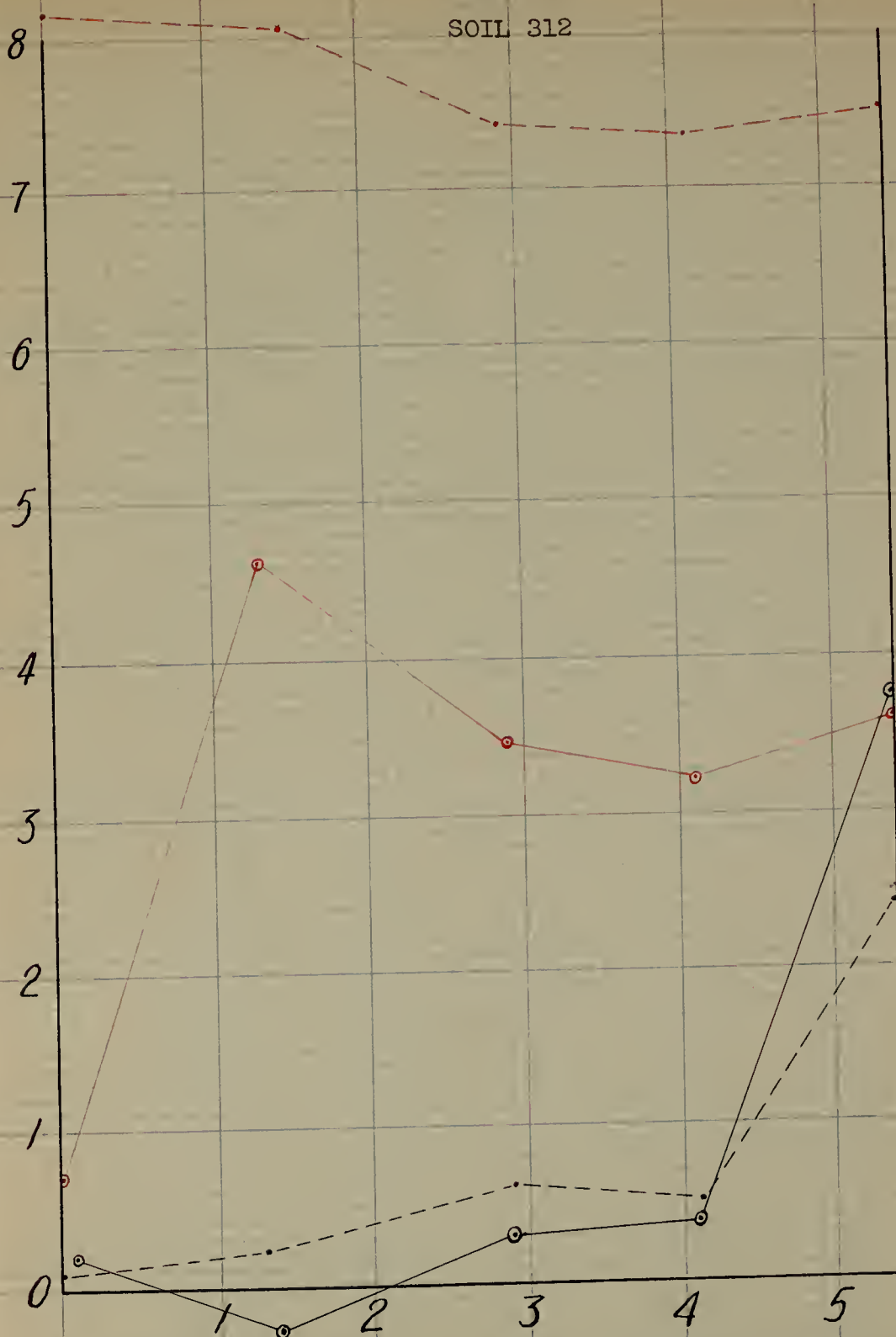


ORDINATES - NO₃-N (·---·); 1 large division = 100 p.p.m.
 NH₃-N (○—○); 1 large division = 100 p.p.m.
 pH (·---·); 1 large division = 1 pH.
 E_h (○—○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 23

SOIL 312

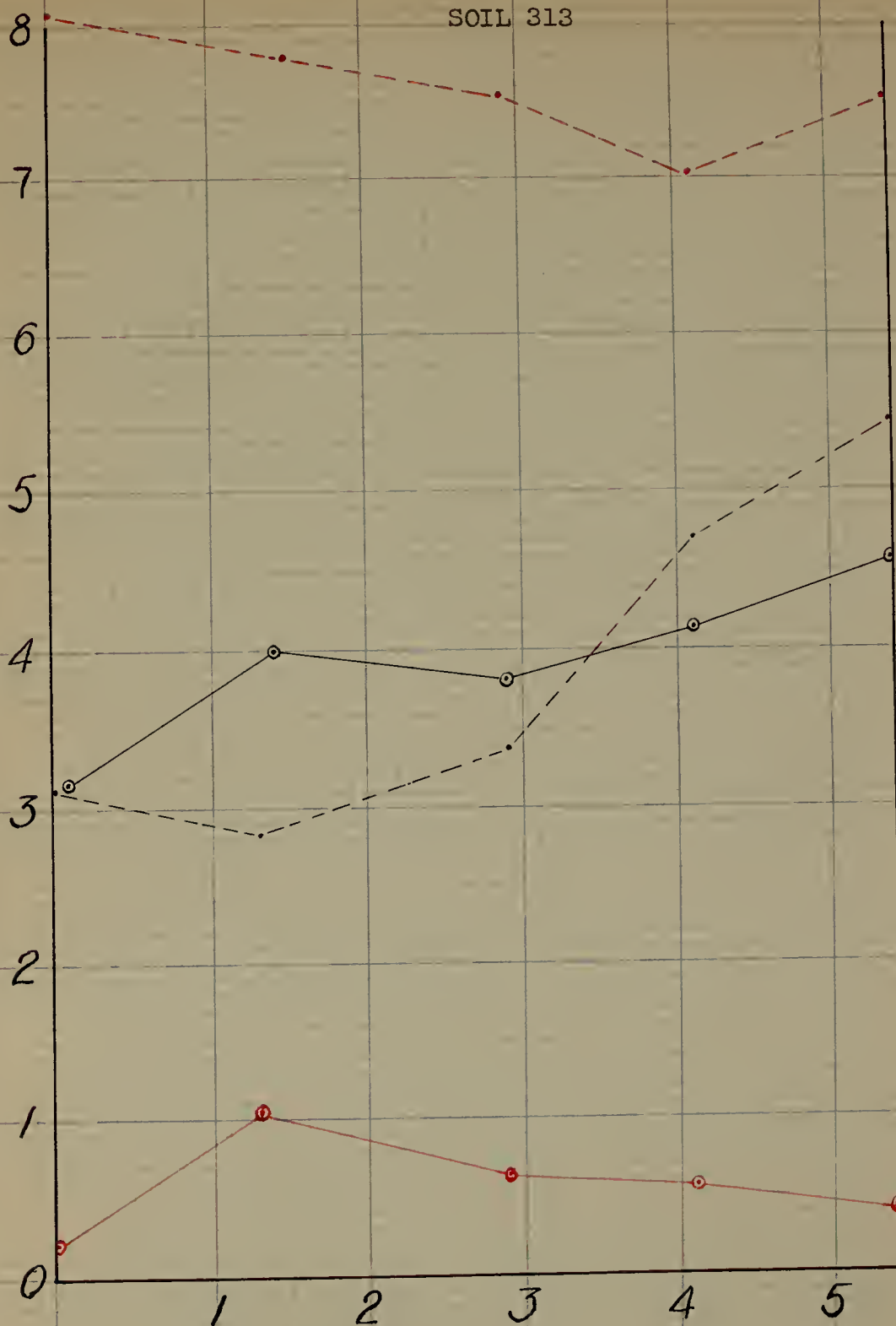


ORDINATES - NO₃-N (·- - -·); 1 large division = 100 p.p.m.
 NH₃-N (○- - -○); 1 large division = 100 p.p.m.
 pH (·- - -·); 1 large division = 1 pH.
 E_h (○- - -○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 24

SOIL 313

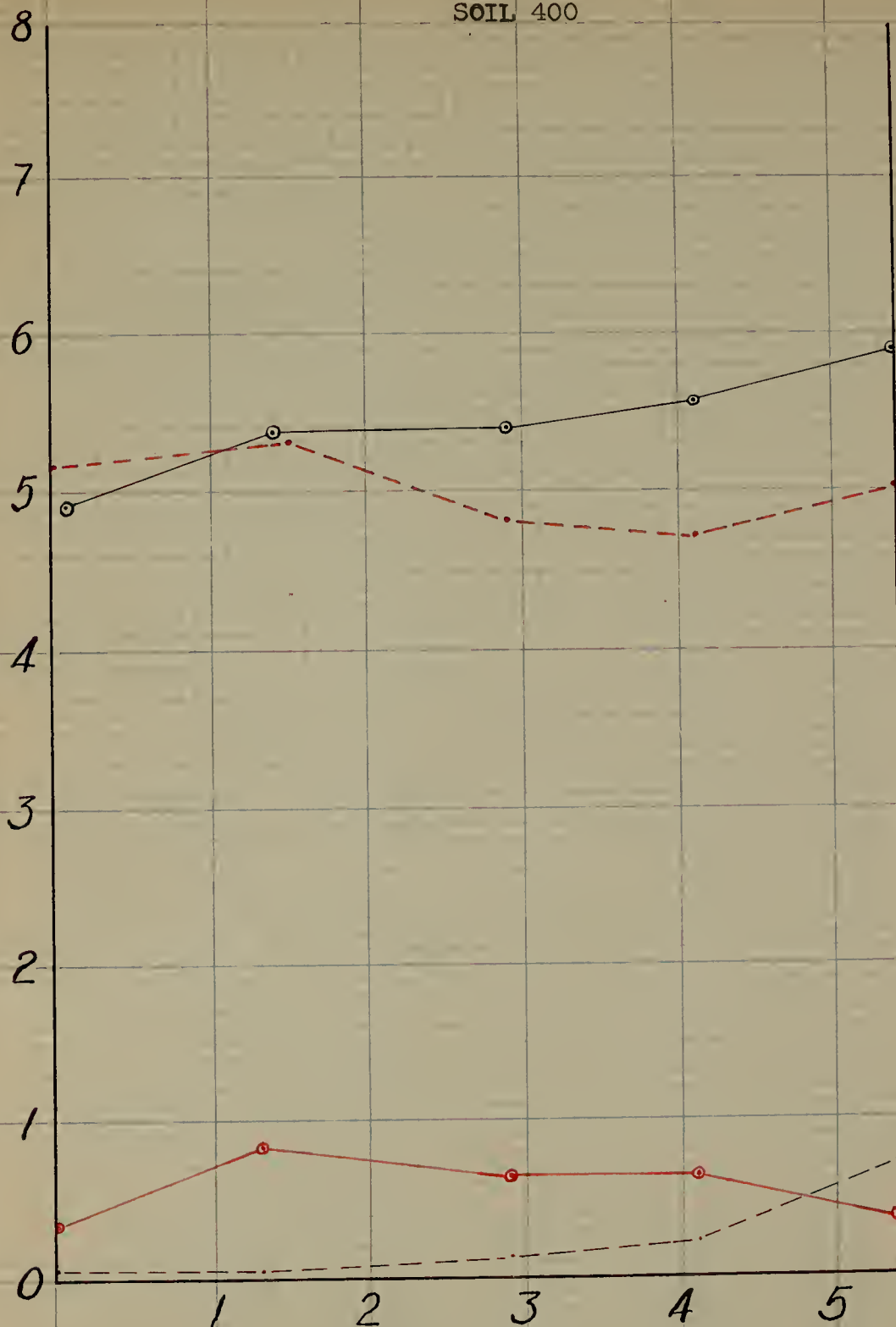


ORDINATES - NO₃-N (·-·-·); 1 large division = 100 p.p.m.
 NH₃-N (○-○); 1 large division = 100 p.p.m.
 pH (·-·-·); 1 large division = 1 pH.
 E_h (○-○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 25

SOIL 400

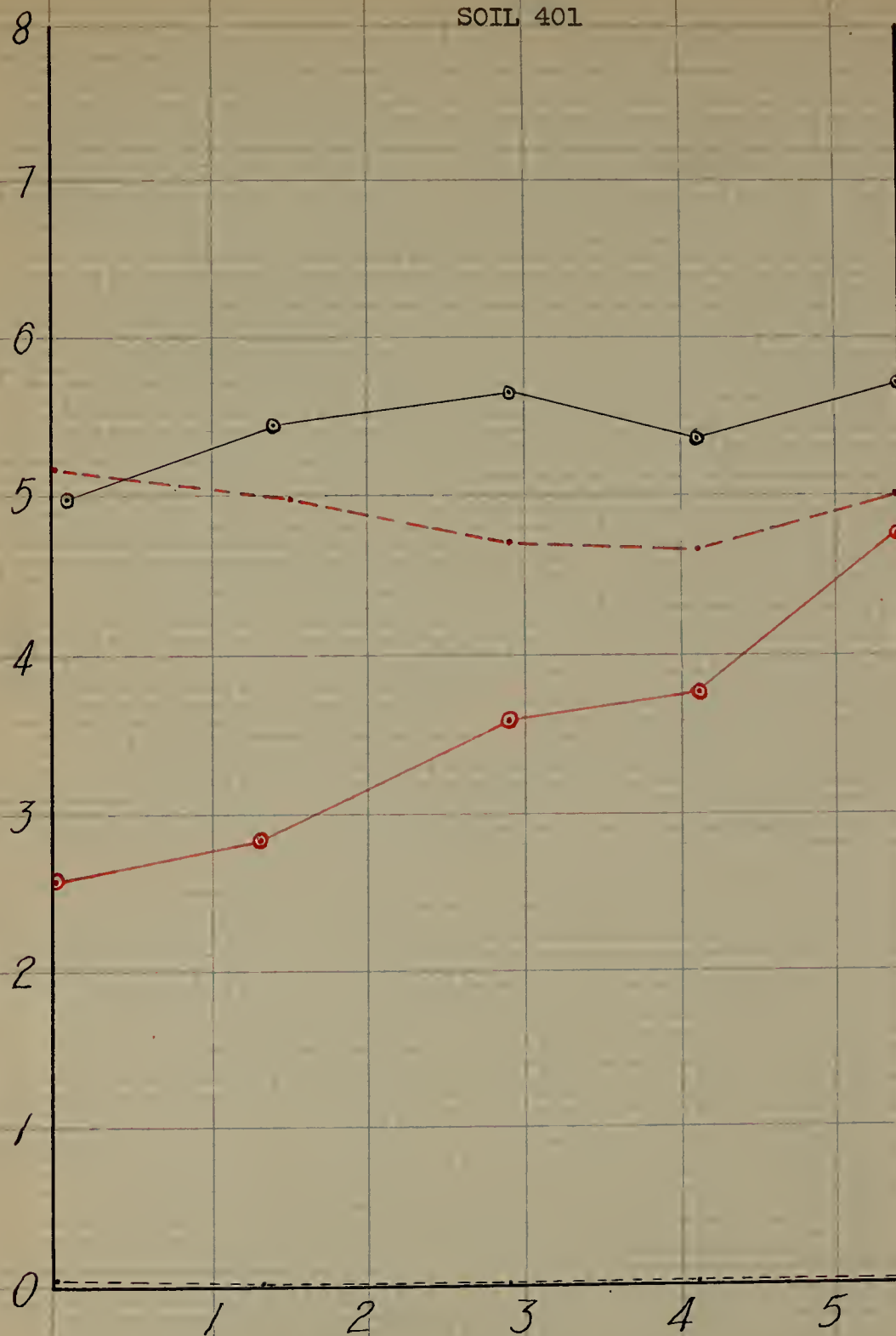


ORDINATES - NO₃-N (·---·); 1 large division = 100 p.p.m.
 NH₃-N (○—○); 1 large division = 100 p.p.m.
 pH (·---·); 1 large division = 1 pH.
 E_h (○—○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 26

SOIL 401

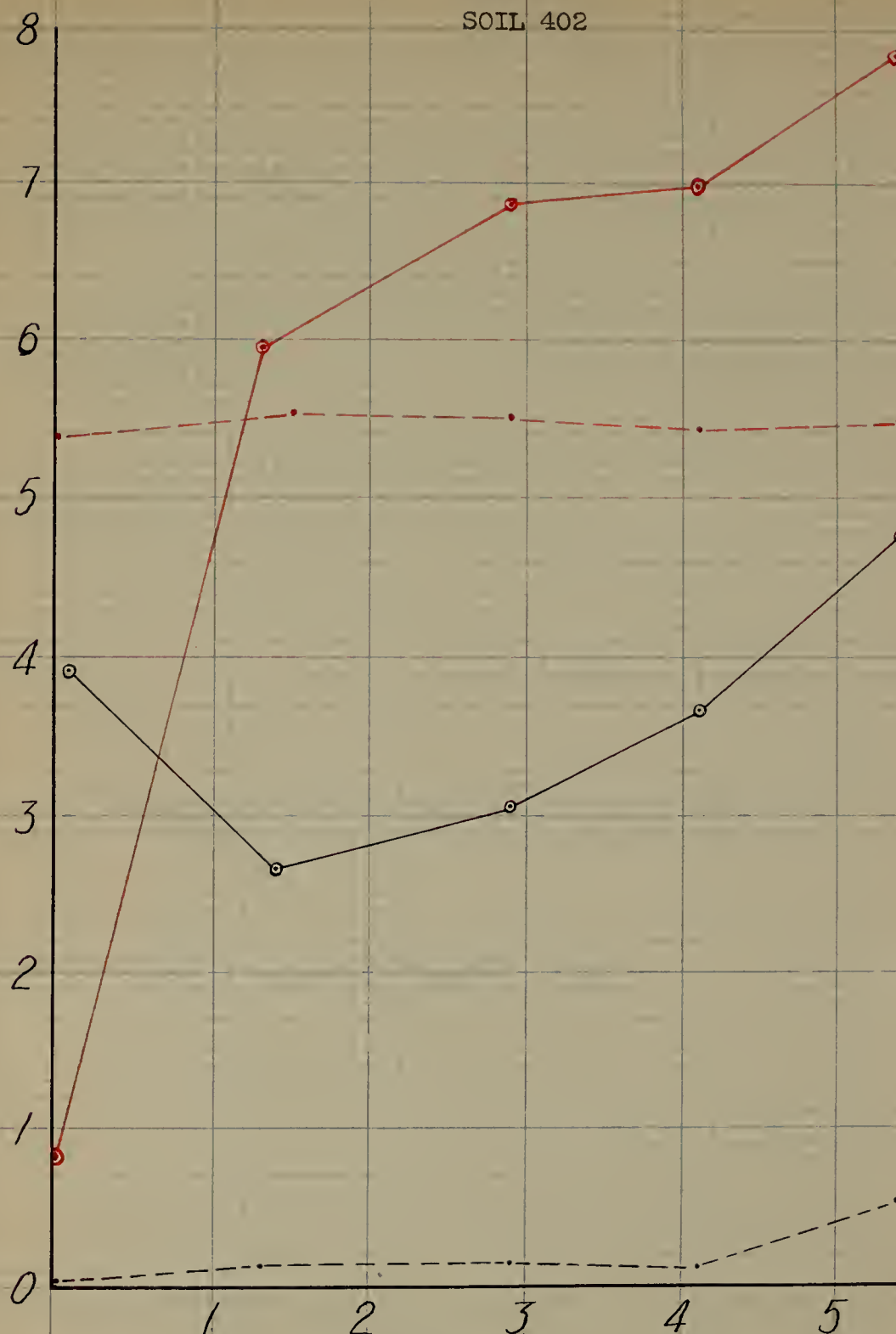


ORDINATES - $\text{NO}_3\text{-N}$ (·---·); 1 large division = 100 p.p.m.
 $\text{NH}_3\text{-N}$ (●---●); 1 large division = 100 p.p.m.
 pH (·---·); 1 large division = 1 pH.
 E_h (○---○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 27

SOIL 402

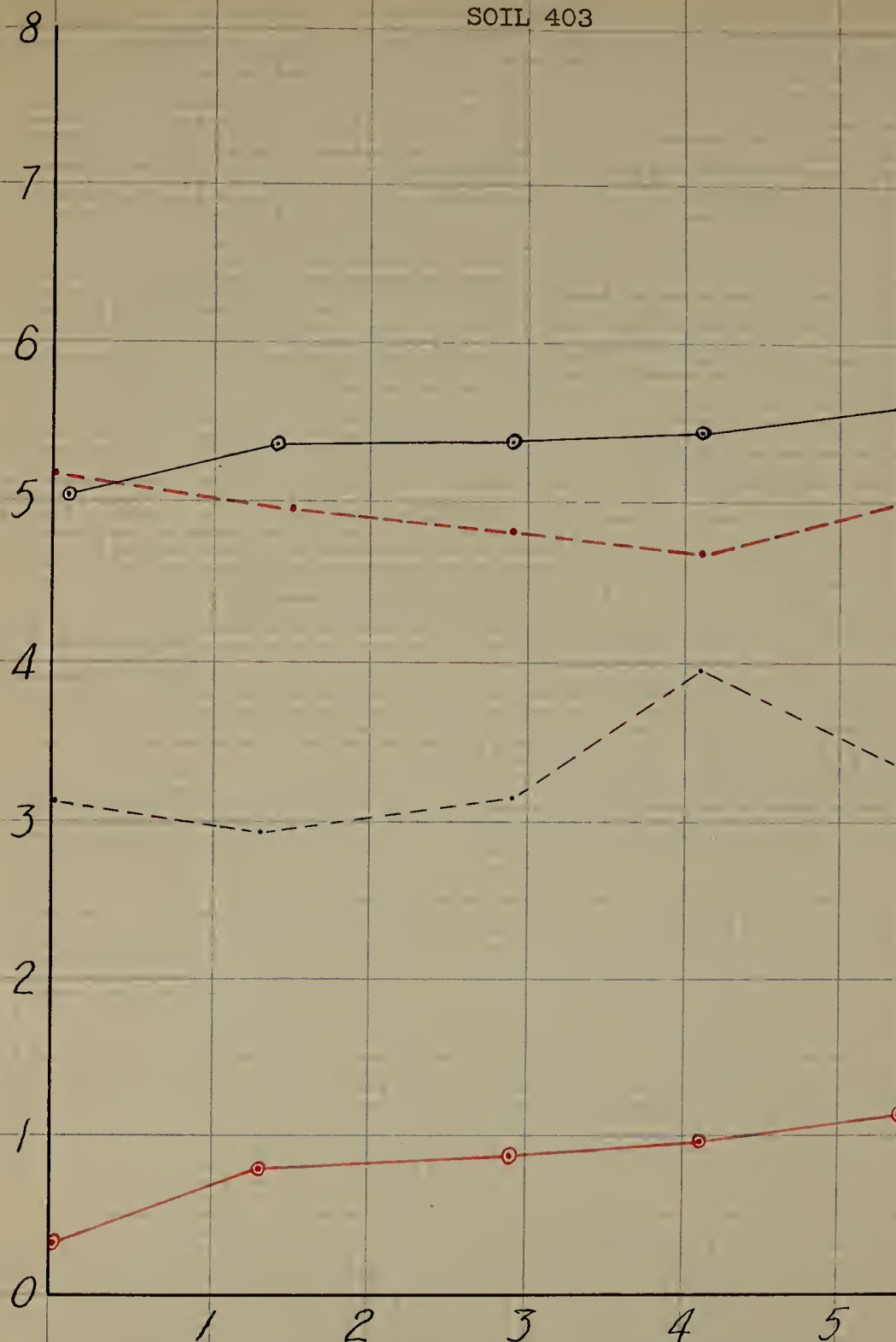


ORDINATES - NO₃-N (·- - - ·); 1 large division = 100 p.p.m.
 NH₃-N (○- - - ○); 1 large division = 100 p.p.m.
 pH (·- - - ·); 1 large division = 1 pH.
 E_h (○- - - ○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 28

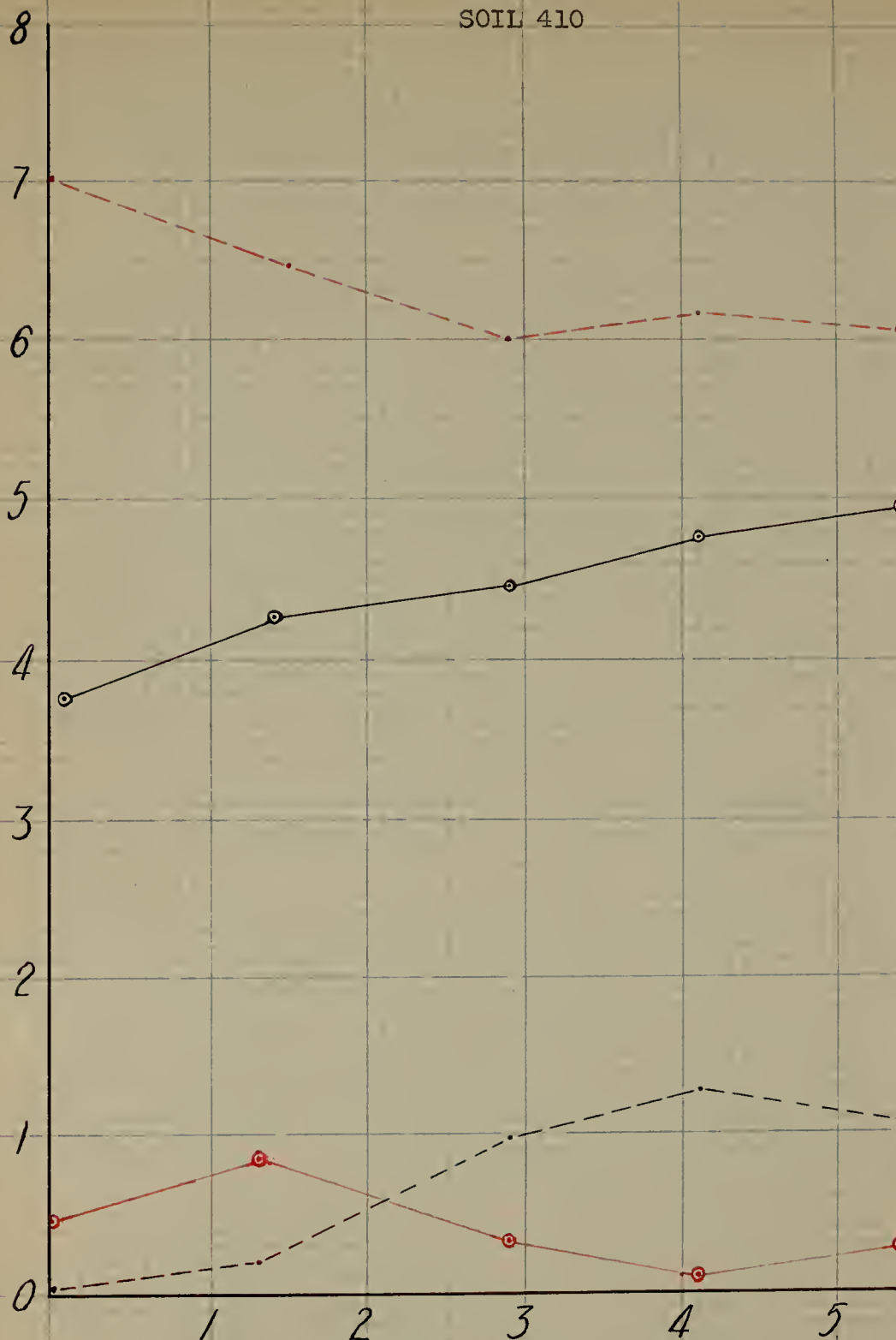
SOIL 403



ORDINATES - NO₃-N (----); 1 large division = 100 p.p.m.
 NH₃-N (—●—); 1 large division = 100 p.p.m.
 pH (---); 1 large division = 1 pH.
 E_h (—○—); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

SOIL 410

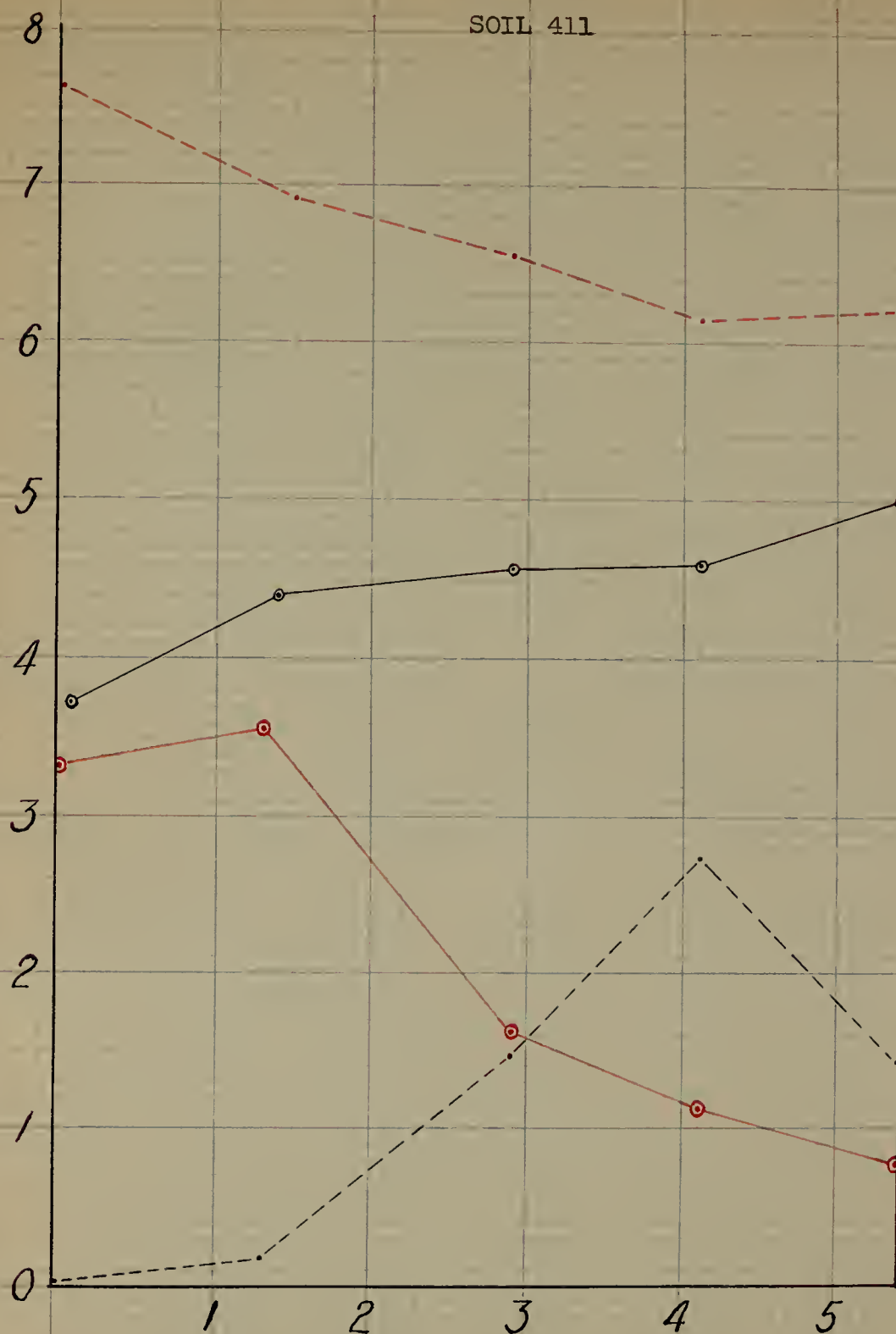


ORDINATES - NO₃-N (---); 1 large division = 100 p.p.m.
 NH₃-N (—○—); 1 large division = 100 p.p.m.
 pH (---•---); 1 large division = 1 pH.
 E_h (—○—); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 30

SOIL 411

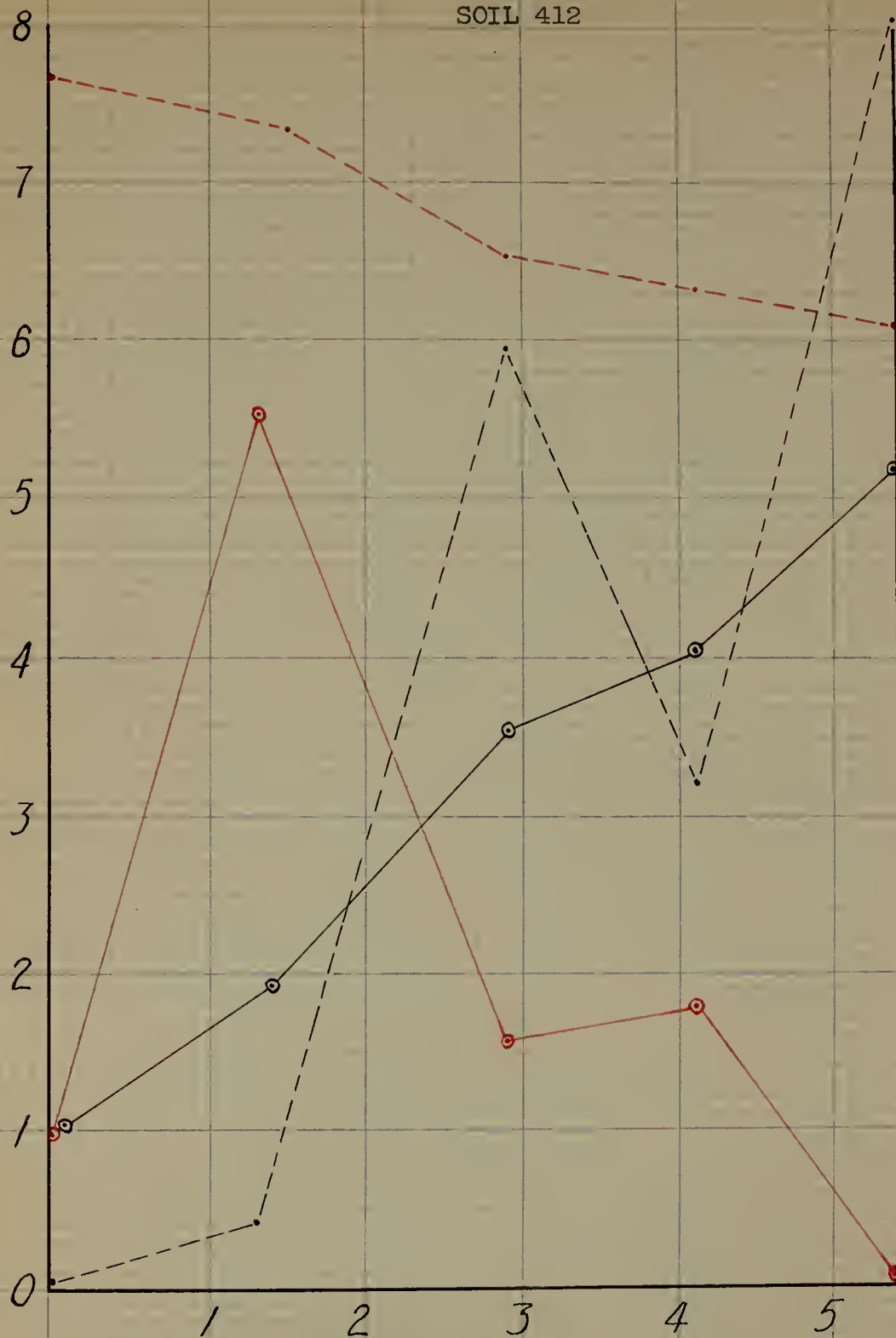


ORDINATES - NO₃-N (·- - - ·); 1 large division = 100 p.p.m.
 NH₃-N (·- - - ·); 1 large division = 100 p.p.m.
 pH (●- - - ●); 1 large division = 1 pH.
 E_h (○- - - ○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 31

SOIL 412

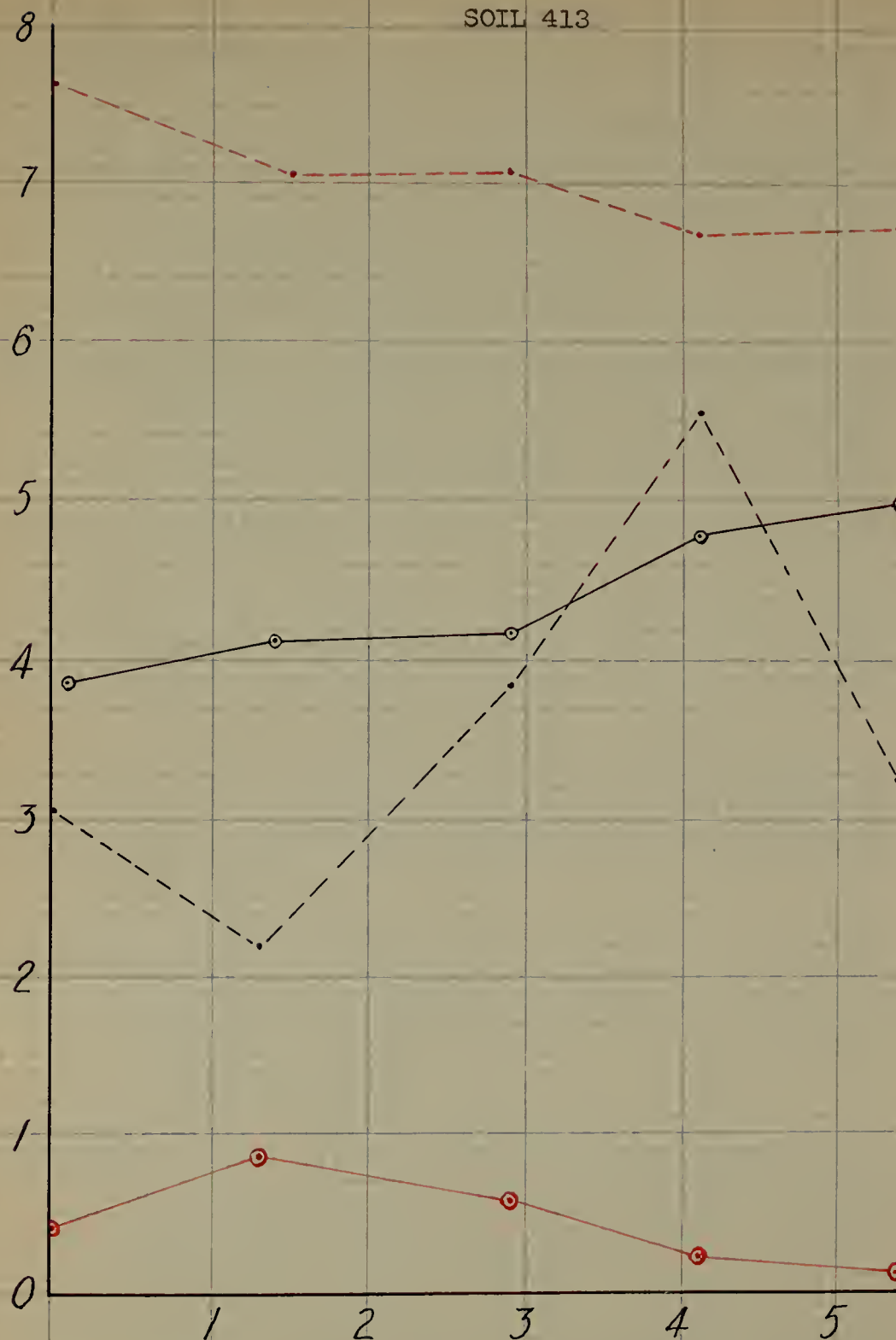


ORDINATES - NO₃-N (·- - - ·); 1 large division = 100 p.p.m.
 NH₃-N (○- - - ○); 1 large division = 100 p.p.m.
 pH (·- - - ·); 1 large division = 1 pH.
 Eh (○- - - ○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

Chart 32

SOIL 413



ORDINATES - NO₃-N (•---•); 1 large division = 100 p.p.m.
 NH₃-N (○—○); 1 large division = 100 p.p.m.
 pH (•---•); 1 large division = 1 pH.
 E_h (○—○); 1 large division = .1 volt.

ABSCISSAS - Time; 1 large division = 10 days.

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VII. ACKNOWLEDGEMENT

The writer wishes to express his appreciation to the members of the committee under whose direction this paper was prepared; to Dr. R.W. Fessenden, of the Chemistry Department for his many timely suggestions; and to the members of the Agronomy Department for their interest and encouragement.

Approved by

Walter S. Eisenmenger

Fred W. Moore

James E. Fuller

Graduate Committee

Date May 31, 1934.

