Oxidation-Reduction Potentials in Rice Soils – Trends in a Dry Zone Field

C. R. PANABOKKE

Introduction

THE earliest work on the study of oxidation-reduction potentials developed in soils was that of Gillespie (1) in 1920. Aspects of this subject have been taken up at various times by different workers, and in some instances their findings have had practical application. The better known investigations are those of Bradfield, Batjer, and Oskamp (2) and of Peech and Batjer (3) on the relation of the oxidation-reduction potentials to fertility in orchard soils, and the work of Pearsall and Mortimer (4) whose findings have been successfully exploited by the Japanese in the manuring of rice by the deep placement of ammonium sulphate. A recent publication on oxidation-reduction potentials carried out in rice soils is that of De Gee (5), where reading were taken *in situ* in a field with rice plants two months old, in order to test the theory regarding the formation of a " sawah " profile (Koenigs, 6).

In the studies carried out in 1952-53, in a rice field at the Agricultural Research Station, Maha Illuppalama, oxidation-reduction potential measurements were made at points down the depth of the profile, at various intervals, starting from the time just prior to transplanting (i.e., a fortnight after flooding). These studies show the trends in depth zonation of the oxidized and reduced layer with time, and suggest certain modifications in the present practice of the application of top dressings of ammonium sulphate.

Theoretical Considerations

A definite potential difference exists between an unattackable platinum wire and a solution containing a mixture of oxidant and reductant which can be brought into a reversible equilibrium. The theoretical expression that equilibrates an oxidation-reduction potential and the system it represents is given by the relation :

$$E_h = E_o - \frac{RT}{nF} \ln \frac{(\text{oxid})}{(\text{reduc})}$$

where E_h = potential in volts referred to the normal hydrogen electrode as zero of the system under consideration,

E_o = constant characteristic of the system,

R = Gas constant,

T = Absolute temperature,

F = Faraday = 96500 coulomns,

n = number of electrons involved in change from oxidized to reduced form,

(oxid) = concentration of oxidized form,

(reduc) = concentration of reduced form.

The electrometric method of measuring this potential consists in building an electric cell in which the system under study is made one half cell, and the other half is any standard cell. The unknown half cell has an unattackable platinum electrode immersed in the system under study. The two half cells are connected by an electrolytic bridge and the electric potential is measured by a potentiometric set up.

The accurate determination of the potential of a soil system is a difficult procedure because the soil is very heterogeneous and contains several distinct oxidation-reduction systems, some of which poise only with difficulty in the presence of biological catalysts. On account of the presence of iron in all soils, one could interpret all potentials of the soil system in terms of the system $Fe^{+++} + e \rightleftharpoons Fe^{++}$ But one cannot avoid the possibility of other systems participating, some of which exist in the colloidal condition and contain many kinds of organic matter oxidizable to different extents. However, in a well-aerated soil where the $Fe^{+++} + e \rightleftharpoons Fe^{++}$ system predominates, the theoretical formulations will hold quite well. Yet the measurement of oxidation-reduction potentials in a paddy soil by a method where the system can be well poised would be very useful.

Experimental Procedure

Gillespie (1) measured the oxidation-reduction potentials of water-logged soils by allowing the platinum electrodes to remain in the soil covered with water and measuring the potential each day. Brown (7) allowed the platinum electrode to remain in contact with a soil-water mixture of fixed ratio, and employed centrifuging of the system to bring about better contact, after which the potential was measured. Both these methods were tried out, but proved unsatisfactory as potential drifts were observed in all cases which had no regularity in behaviour to permit a system of standardization. The measurement of the potential of a water-logged soil when suspended in 0. 1 N sulphuric acid proved to be the most satisfactory as the systems were well poised at this pH, and hardly any potential drifts were observed after standing for 30 minutes. As all results were to be transformed to the E_h at (pH = 7) scale, the pH – E_h relationship was determined by measuring the Eh at various pH values of the soil in 0. 1 N sulphuric acid. A pH – E_h slope of 0.07 volts per unit change in pH was obtained, which held constant for the soil at all respective depths down the profile.

The platinum electrodes which were cleaned with hot chromic acid, rinsed in distilled water and heated over an alcohol flame, were placed in the 0. 1 N sulphuric acid soil suspension, and the tube containing the soil was well tapped to ensure good contact between the soil and the platinum electrode. After standing for 30 minutes contact was made with a standard (silver/silver chloride) electrode through an agar bridge and a potentiometric set up, which measured the electric potential of the cell. A pH determination was also made of every sample after the E_h determination, and the E_h was corrected to E_h at pH = 7. The soil samples were collected in the field from the respective depths down the profile into small, darkened, air-tight bottles with minimum delay. The manner of drawing the sample was to scoop out a soil monolith lying between two points (say 5—7 cms. from the surface) with the aid of a spatula from a freshly cut face of the profile, and the E_h value of the sample from this zone is designated to that at a point 6 cms. from the surface. The surface samples were taken by gentle superficial scooping of the surface.

From a field which was transplanted on November 24, samples were taken on November 23 (i.e., a day prior to transplanting) and again on December 8, to a depth of 100 cms. down the profile. Thereafter samples were taken to a depth of only 15 cms. on the following dates:—December 27, January 3, January 11, January 20 and January 27. A shortage of irrigation water due to failure of rains curtailed progress beyond this stage.

Results and Discussion

Readings taken on November 23 and December 8, 1952, which are represented in curves A and B of Fig. 1, show the trend in the building up of the oxidation-reduction potential profile at the early stages. An increase in value of the surface layer from a potential of -10 millivolts to $+50$ millivolts, together with an overall increase in the oxidation-reduction potential over the whole length of the furrow slice, has occurred within the period of the first two weeks. The shape of the curve also indicates that oxidative conditions prevail below the furrow slice. Such oxidative conditions could be associated with good sub-soil drainage.

In curve C (Fig. 2) which represents the reading on December 20, it is observed that the potential of the surface has increased to a value of $+290$ millivolts. The above trend in the development of the oxidation-reduction potential curve could, to a certain extent, be explained on the existing knowledge of the behaviour of paddy soils. When a paddy field is flooded with irrigation water, the microbiological balance in the soil is considerably altered. Under the resulting anaerobic conditions, the heterotrophic organisms which decompose organic matter and consume oxygen, give rise to reduced conditions in the puddled section of the furrow slice. In course of time, however, the water which is charged with oxygen both from the atmosphere and from the hydrophytic plant associations, influences the uppermost layer of the paddy soil, and conditions favourable for the growth of the autotrophic organisms in this layer result. The enhancement of the autotrophic activity with time is reflected in the rate of building up of the oxidation potential of this layer.

It is known that when ammonium sulphate is applied to the surface of the paddy field the ammonium nitrogen is oxidized to the nitrate nitrogen by the aerobic organisms. This nitrate nitrogen on leaching downwards undergoes de-nitrification by the anaerobic organisms and ultimately escapes as free nitrogen. From the trend in the oxidation potential values so far observed, it appears that the oxidation of ammonium nitrogen at the surface which will be slow in the initial stages, would be greatly intensified with time. A cultural practice which could incorporate the ammonium sulphate in the reduced section of the furrow slice, at the time of application of top dressing, is accordingly desired.

The determinations made on December 27, 1952, January 3, 11, 20 and 27, 1953, cover the period between the phase of tillering and the phase of initiation of inflorescence primordia, and are represented in curves D and E (Fig. 2), F, G and H (Fig. 3). The sequence indicates a breaking up of the furrow slice into several zones where alternate oxidative and reductive conditions prevail.

Evidence supporting the view of a downward diffusion of oxygen (8) may be found in the overall rise in the oxidation potential of the reduced layer. In the early stages, under the prevailing conditions of equilibrium, the furrow slice is composed of a thin superficial oxidized layer and a broad reduced layer beneath it. This situation gradually undergoes transformation on account of certain other operative factors asserting their influence. The diffusion of oxidative substances from the roots of the rice plant (9) will influence the equilibrium in the reduced section of the furrow slice. Moreover, a peculiar development of the profile in the flooded furrow slice of a paddy soil (8), explainable on the principle governing the Liesegang phenomenon, where a downward diffusion of oxygen followed by certain physico-chemical changes ultimately results in the formation of thin bands of ferric hydroxide down the profile, is corroborated by the evidence borne out in the shape of the curves: D, E, F, G and H.

Conclusions

In the development of the oxidation-reduction potential profile, certain factors manifest themselves. Microbiological activity is followed up by the diffusion of oxygen from the surface of the soil and from the roots of the rice plant. These processes running parallel to each other and acting in unison, give rise to a system of equilibrium initially simple and finally complex.

An increase in the value of the oxidation potential of the surface layer with time is observed. The importance of incorporating the ammonium sulphate in the reduced zone of the furrow slice at the time of the top dressing is indicated.

Acknowledgements

The author is grateful to Dr. M. F. Chandraratna at whose request this investigation was undertaken. He is also indebted to Mr. E. Abeyratne for his valuable suggestions throughout the course of the investigation, and to Mr. T. Kanthasamy and Mr. N. Kanaganayagam for their help in carrying out the experiments. Thanks are also due to Dr. Devanadan of the Physical Chemistry Department of the Ceylon University for the loan of apparatus and accessories.

Literature Cited

(1) GILLESPIE—*Soil Science*, 1920.

(2) BRADFIELD, BATJER and OSKAMP—*Cornell University Agriculture Expt.* Sta. Bull. 592.

(3) PEACH and BATJER—*Cornell University Agriculture Expt.* Sta. Bull. 625.

(4) PEARSALL and MORTIMER—*Journal of Ecology.* 27. 1939.

(5) DE GEE—*Contributions of Central Agric. Station*, Bogor, 106.

(6) KOENIGS—*Contributions of Central Agric. Station*, Bogor, 105.

(7) BROWN—*Soil Science*, 1934.

(8) SHIORI and TANADA—*Chemistry of paddy soils in Japan. International Rice Commission, Working Party on Fertilizers, Bandung*, 1952 IRC/FP/52/43.

(9) VAN RAALTE—*Ann. Bot. Gardens' Buitenzorg.* 1940.

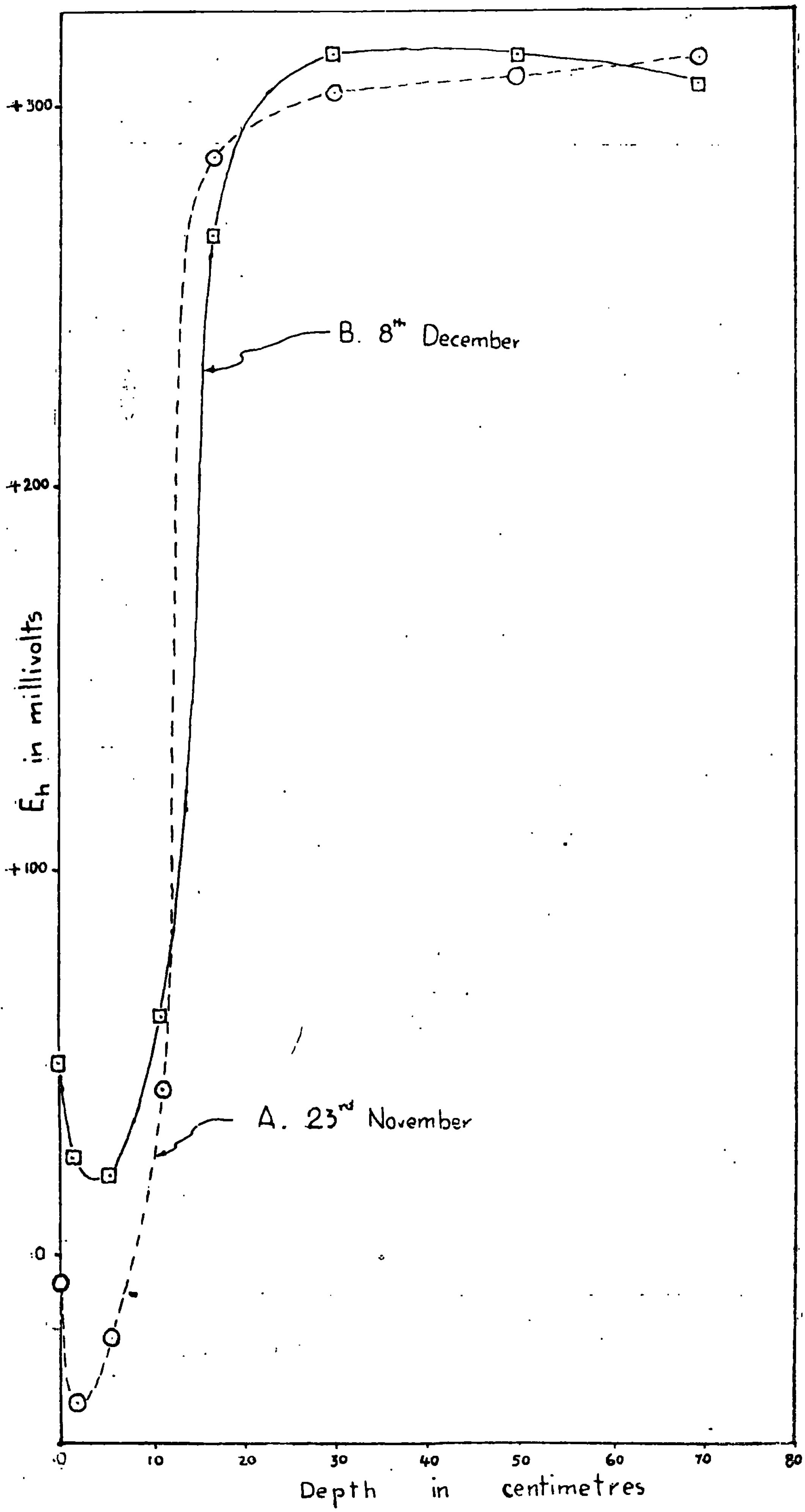
+300
+200
+100
0
B. 8th December
A. 23rd November
Eh in millivolts
0
10
20
30
40
50
60
70
80
Depth in centimetres

Fig. 1

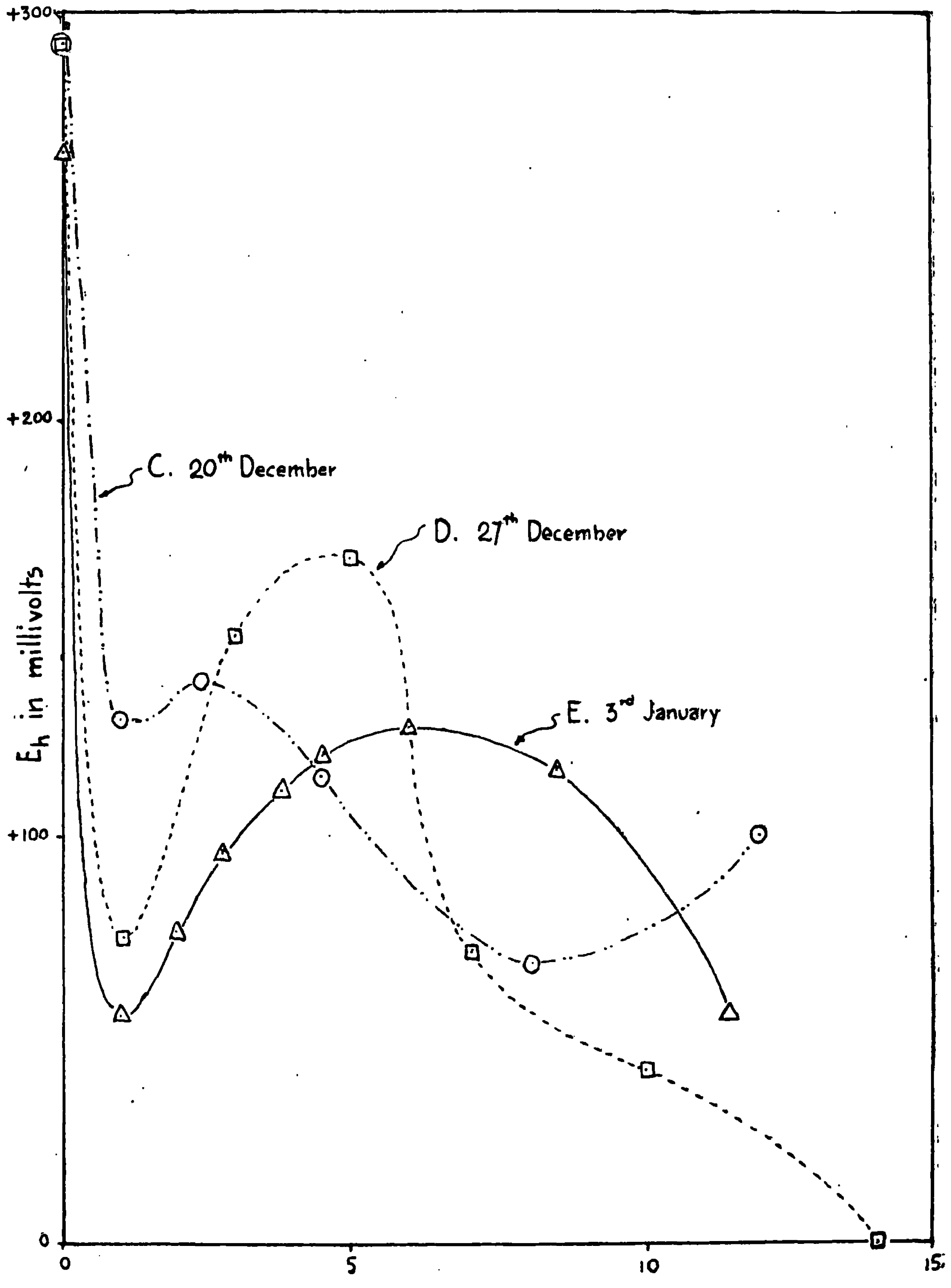
+300
+200
+100
0
Eh in millivolts
0
5
10
15
Depth in centimetres
C. 20th December
D. 27th December
E. 3rd January

Fig. 2

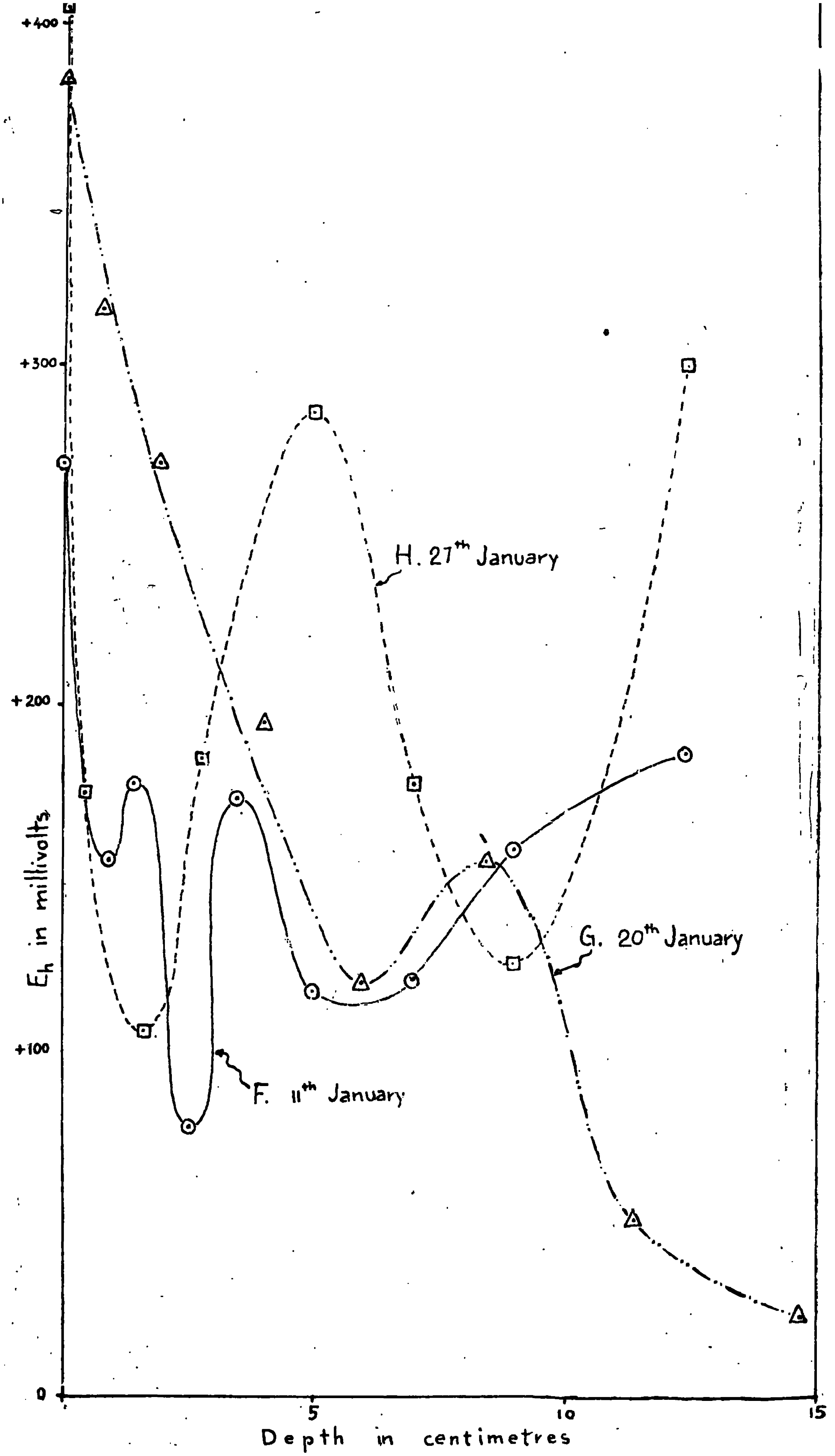
+400
+300
+200
+100
0
0
5
10
15
Depth in centimetres
Eh in millivolts
H. 27th January
G. 20th January
F. 11th January

Fig. 3