

Short communication

437 — SOIL REDOX POTENTIAL AS A CHARACTERISTIC INTENSITY VALUE OF THE ACTIVE PROCESSES IN BIOGEOCENOSIS

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INTRODUCTION

In the literature a large quantity of data has been gathered on the determination of the redox potential (U_h) for different soils. However, theoretical aspects connected with interpretation of the results of measuring U_h , as well as problems of further application of the available data, are not sufficiently developed [1-4]. In the previous report [5] we used a thermodynamic approach to analyse the seasonal dynamics of the U_h value of the steppe biogeocenosis. The objective of the present work is further development of the idea of the redox potential as the value characterizing the state of the active processes in the biological systems.

Experimental

The measurement of the redox potential was carried out under the plant association (*Stipa lessingiana* + *Festuca sulcata* + *Herba varia*) of the Azov Sea region steppe (an ordinary chernozem).

A thin-layer platinized electrode was used as a working electrode and a saturated Ag|AgCl electrode as a reference, connected with a field pH meter (fabricated at the Gomel Plant for Measuring Instruments) as an indicating instrument. The U_h values are given versus the normal hydrogen electrode.

The working electrodes were immersed in soil in five points of the phytocenosis (2-3 electrodes in each point) to a depth of ~7 cm for the whole measuring period (5-7 days). The reference electrode was immersed only for reading to avoid soil contamination with potassium chloride. The U_h value of the soil was recorded 2-3 days after immersion to ensure contacts with all the components of the soil.

During the growing periods of 1977-78 the U_h values were determined at the following times:

* Electrochemistry.

** Soil Science.

(1) the end of March to the beginning of April 1977, before the mass vegetation;

(2) the first half of May, the period of vigorous growth of the green mass vegetation;

(3) the end of June to the beginning of July;

(4) the end of July to the beginning of August;

(5) the second part of November, cessation of vegetation growth;

(6) the beginning of April 1978.

In view of the fact that earlier [6] a steady daily rhythm of the U_h value was established for the soil of a steppe biogeocenosis, each point (Fig. 1) shows an average value from the observations 3–4 days, when 12–15 electrodes were read six times a day from 6 a.m. to 9 p.m. with an interval of 3 h. This approach ensures a good reproducibility of an average value of U_h (± 3 –5 mV). Parallel to the U_h control we determined the field moisture capacity of the soil by the weight method and the soil temperature; the soil solution was forced out with ethyl alcohol according to the procedure described in Ref. 7.

RESULTS AND DISCUSSION

Figure 1 shows a time-dependent curve for the soil redox potential. As already shown [5] this curve is in good agreement with the principles of thermodynamics of irreversible processes for open systems [8–10]. This provides for a presentation of the measured U_h values of the soil as the intensity characteristic of the active processes occurring in the given biological system (the topsoil layer in the steppe biogeocenosis).

The examples given below prove these suppositions. Thus, Fig. 2 shows a change in the potential after cathodic and anodic polarization of the working

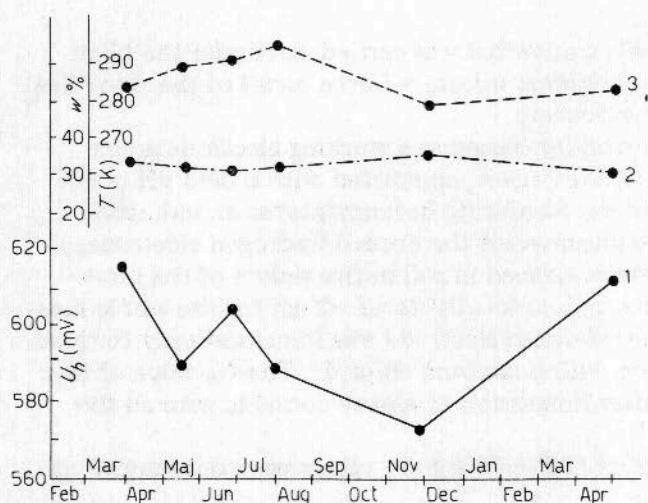


Fig. 1. The variation dynamics of the soil redox potential in the steppe biogeocenosis, U_h (1), and the corresponding values of soil moisture capacity, w (2), and temperature, T (3) during the growing period.

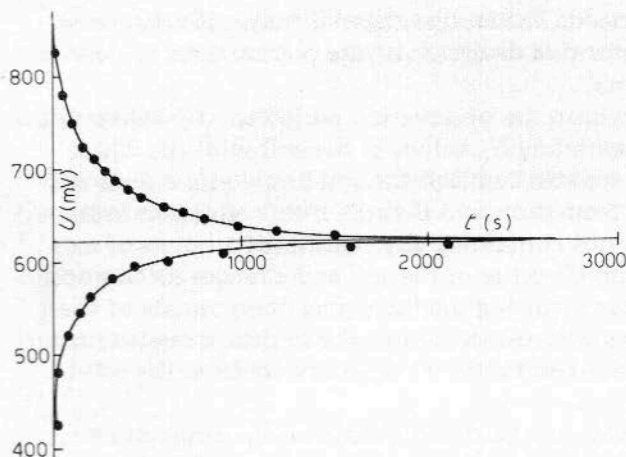


Fig. 2. The decay curves of the potential of the platinized electrode after cathodic and anodic polarizations in ordinary chernozem (*in situ*).

electrode in an ordinary chernozem at the current density $j = 2 \text{ mA/cm}^2$ carried out according to the procedure given in Ref. 11. The potential returns to the rated value in both cases. Maintenance of the given condition is considered as an indication of an unbiased electrode reading in the biological environment [11].

On the other hand, it is known that in soils, in general, and in the soils of the Azov Sea region which is not considered to be the area of iodine endemism in particular, iodine compounds of different active valences are available. The results given in Ref. 12 show that in subsoil water of the region studied genetically related to the soils, the iodine content amounts to $(4-10) \times 10^{-6} \text{ g/dm}^3$. It is also known that for objects of this type where the redox reactions involve organic compounds of a complicated composition, potential mediators are used. They are actually simple redox systems, for example I^0/I^- [13] at concentrations close to those observed in the soils investigated ($10^{-6}-10^{-8} \text{ M}$), and not affecting the potential of the system under investigation. These mediators make the metal electrode capable of assuming a value of the potential corresponding to that of the system investigated. The latter should be related to the reference potentials of some redox reactions occurring in soil [14].

Thus, the results of the polarization of the electrodes and the presence of potential mediators in soil make it possible to show unequivocally that the assigned U_h value reflects a true value of the irreversible non-equilibrium redox potential of the soil; moreover, it is numerically equal to the reversible redox potential of the mediator system [15].

Among many major questions requiring answers to ascertain the reasons causing U_h fluctuations in the system, one can note the following: What is the role of various parts of a complicated object in the creation of the corresponding redox conditions?

In our studies, at the same time as measuring U_h values of the soil, we observed fluctuations of the potential of the platinized Pt electrode in the soil

solution during the growing period. The studies showed that, within experimental error, there was no substantial deviation of the potential from a certain mean value equal to 480 mV.

It seems worth noting that within the observation period the U_h values in the soil were larger than the corresponding U_h values in the soil solution. These data at least give reasons for a supposition that the soil liquid phase does not have a dominant effect on the formation of a definite redox situation in the soil. The soil moisture, though not containing any significant amount of substances, indirectly influences the U_h value of the soil and changes its composition, depending on the processes involving the biological components of the soil, its solid and gaseous phases with due regard to the hydrothermal regime, irregularity of leaching of oxidized and reduced components from the solid substrate, etc.

Thus, for example, the experiments on determining the U_h value under different conditions showed that after 32.5 mm precipitation (with the increase of soil moisture capacity from 21.2 to 34.5% after rain) the U_h value (*in situ*) dropped from 592 mV to 576 mV, and after two sunny days it rose again to 592 mV, although the soil moisture capacity decreased only to 32.1%. Consequently, we may conclude that the soil solution considered as part of the whole object, is a conducting medium, transferring the variations of the redox situation from the soil living substance to the electrode surface, as is assumed in the experiments with microbiological media [16] and with the deposits of mineral oils [17]. In the literature [2] there are also statements in favour of the preferential influence of the solid part of the soil on U_h .

On the basis of a general assumption it should be added that, from our viewpoint, in the natural state * the time-dependent tendency of the U_h value is primarily determined by the soil living substance, whereas the quantitative conditions for U_h are determined by the combination of many natural factors (including the organic and mineral composition, aeration, etc.).

In conclusion we would like to point out that the practice of utilization of the redox potential to characterize the active processes in the soil could be applied to other biological objects, and with improvement of the theory and of experimental methods the U_h value could become an efficient tool for revealing any deviation from normality in the natural processes, whether or not this deviation is caused by natural or anthropogenic activities.

CONCLUSIONS

- (1) The value of the soil redox potential can thermodynamically characterize the active processes in the biogeocenoses under certain conditions (special-purpose measuring techniques and the availability of the potential mediators).
- (2) The liquid phase of the soil (the soil solution) has no dominating effect on the formation of the redox situation in the object investigated, and plays the part of the interceding medium in the chain solid-phase electrode.

* Under agrocenosis conditions human activities (application of fertilizers, use of herbicides, irrigation, etc.) may greatly affect the U_h value of the soil [18].

(3) The dynamics of the redox potential in the undisturbed soil is determined, to a considerable extent, by the soil biological components.

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