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Effect of corona discharge plasma on redox processes in soil

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Studies have been conducted on the effect of corona discharge plasma on redox reactions of the soil, namely on samples of lowland peat (capillary saturated with water) and pure quartz sand (air-dry) in pure form and in mixtures with different ratios of peat and sand. Discharge parameters: duration up to 60 minutes, discharge voltage $U = 10\text{--}20$ kV, discharge current $I = 20\text{--}100$ microA. A maximum effect of the corona discharge treatment of the samples has been obtained in relation to the redox potential. The process of oxidation of organic matter is under the influence of ozone and negative ions in the plasma of the corona discharge. The effectiveness of the negative corona is 2–5 times higher than of the positive one and is connected with more effective production of negative ions.

Keywords: corona discharge; redox reactions of soil; lowland peat; pure quartz sand.

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Introduction

The oxidation-reduction potential (redox, ORP) is widely used in scientific research for characterizing soil conditions (moisture, pH, soluble compounds, etc.) [1–6]. Soil ORP is extremely responsive to changes in soil formation conditions, melioration measures, and agricultural practices. For example, liming of acidic soils, plowing, and construction of open drain ditches cause a significant increase in ORP in soils. Conversely, soil compaction, grass sowing, and organic manuring reduce ORP. A pair of electrodes buried in the soil mass or in an extracted soil solution generates a potential difference due to the presence of various redox systems in soil layers, which magnitude depends on the concentration and ratio of oxidizing and reducing agents formed during the soil formation process. This potential difference is convenient as a consolidated figure for the redox potential of a given layer or solution in terms of millivolts. ORP describes the level of activity of reactions involving the transfer or attachment of electrons

[1, 6]. In general terms, a redox reaction can be represented as follows [1]: $\text{Ox} + n\text{e}^- \rightarrow \text{Red}$, where Ox is an oxidizing agent; n is a number of electrons involved in a reaction; e^- are electrons; Red is a reducing agent. Some substances lose electrons and get oxidized (oxidation reaction), while others attach electrons and get reduced (reduction reaction). Most oxidation reactions of organic substances are irreversible.

A subject of scientific interest is the use of cold corona discharge plasma to stimulate ORP as a factor in soil development over time under artificial conditions. This research continues our series of studies regarding the impact of corona discharge plasma on biological objects [8, 9]. The synergistic effects of cold plasma on plants and soil are of significant interest. These issues become particularly relevant when studying the possibility of establishing human habitats in extreme conditions. For this reason, one of the objectives of this paper was to conduct experiments evaluating the impact of corona discharge on ORP in soil.

Objects of the Study

The objects to be studied were samples of lowland peat (capillary-saturated with water) and pure quartz sand (air-dried), both alone and as mixtures with varying peat-to-sand ratios.

Characteristics of the objects of the study:

1. Peat. Peat type: lowland. Peat variety: reed. Degree of peat decomposition: 45.0 %. Botanical composition of the peat sample: reed – 50–55 %, deciduous wood – 15 %, pine bark – 5 %, birch bark – 5 %, bogbean (*Menyanthes*) – 5 %, horsetail – 5 %, unknown herbaceous remains – 10 %.

2. Peat + medium-grained quartz sand mixtures:

2.1. Pure peat, 100 % wt. of sample, ash content: 10.5 % (89.5 % organic matter, 10.5 % mineral part).

2.2. Peat + sand (78.6 + 21.4) % wt. of sample (70.3 % organic matter, 29.7 % mineral part).

2.3. Peat + sand (50 + 50) % wt. of sample (44.25 % organic matter, 55.75 % mineral part).

2.4. Peat + sand (21.4 + 78.6) % wt. of sample (19.2 % organic matter, 80.8 % mineral part).

2.5. Pure medium-grained quartz sand, 100 % (100 % mineral part).

Methods of study and Experimental Setup

Samples weighing 70 grams were treated both with negative and positive corona discharge plasma ($U = 10\text{--}20\text{ kV}$, $I = 20\text{--}100\text{ }\mu\text{A}$) for 60 minutes. The corona discharge was selected based on data indicating its air plasma is rich with ions and its known properties, commonly utilized in practice for ozone generation [10]. After treatment, one portion of the samples was brought to a paste-like consistency for measuring the specific electrical conductivity parameter. Another portion of the samples was placed in flasks where distilled water at a soil-to-water ratio of 1:5 was added. The flask was shaken for 10 minutes and filtered through a paper filter. The filtered samples of the water extract from the soil were analyzed for specific electrical conductivity and ORP value. The ORP value was measured in the water extract (1:5) from the samples using an ORP analyzer during the experiment. The electrical conductivity of the

soil pastes was determined using Land Mapper instrument [7].

A schematic of the experimental setup for treating soil samples with corona discharge is detailed in papers [8, 9]. The setup consists of a cell filled with soil samples and an electrical circuit. The upper electrode was a multi-needle system (29 needles) with a needle tip radius of 0.4 mm. The needles were positioned 5–15 mm above the sample surface. The cells were made of either metal or dielectric material. The discharge current was measured with a milliammeter, and the voltage was measured using a circuit comprising resistor R_1 and a milliammeter. The current-voltage characteristics of the discharge above the soil surface were measured.

The drift time t of the generated ions in the corona discharge electric field is approximately [11] $t = x/v = 5 \times 10^{-7} - 5 \times 10^{-6}\text{ s}$, where x is the distance from the needle electrode to the soil surface (5–7 mm), and $v = 10^5\text{--}10^6\text{ cm/s}$ is the ion drift velocity. This time is significantly shorter than the typical soil treatment duration. The active particles generated in the air plasma rapidly move towards the soil surface due to diffusion. The characteristic diffusion time t_D is equal to [12], $t_D = x^2/D$, where D is the ion diffusion coefficient (typical diffusion coefficients are: O_2^- in oxygen – $0.83\text{ cm}^2/\text{s}$, O_3^- in oxygen – $0.056\text{ cm}^2/\text{s}$, $\text{N}_2\text{--O}_2$ atoms – $0.182\text{ cm}^2/\text{s}$). The characteristic diffusion time for particles generated in the plasma to reach the soil surface ranges from 0.3 to 1 s, which is also much shorter than the plasma treatment time. Therefore, the generation of active particles in the air by the corona discharge, which influence ORP of soil can be considered a significant factor of the plasma impact.

Results of Experiments Using Negative Corona

Table 1 presents the parameters of the negative corona discharge.

Table 2 provides specific electrical conductivities of the soil paste.

The organogenic sample exhibits the maximum specific electrical conductivity equaling to $1174\text{ }\mu\text{S/cm}$. As the mineral component of the samples increases, the electrical conductivity decreases. It is minimal in pure sand and equals $68\text{ }\mu\text{S/cm}$.

Treatment of the samples with corona discharge leads to an increase in the specific electrical conductivity (Table 2). As the organic component fraction in the samples decreases, the influence of treatment on the electrical conductivity weakens. The influence of the sample treatment on the electrical conductivity growth was also observed in pure sand.

Table 3 presents the results of measuring the redox potential and specific electrical conductivity of the water extract.

The same pattern of the influence of sample treatment with corona discharge was observed during measurement of the water extract's electrical conductivity (Table 3).

Table 1

Negative corona discharge parameters

Sample	Average current, μA	Average voltage, kV	Average energy, J
Peat 100 %	39	7.5	108
Peat + sand 78.6 + 21.4	107	8.6	331
Peat + sand 50 + 50	160	7.7	444
Peat + sand 21.6 + 78.6	146	10.4	547
Sand 100 %	210	7.3	551

Table 2

Specific electrical conductivity of the soil paste

Sample	EC check (without treatment), $\mu\text{S/cm}$	EC treatment, $\mu\text{S/cm}$	ΔEC , $\mu\text{S/cm}$ (as compared to the check)
Peat 100 %	1174	1300	126
Peat + sand 78.6 + 21.4	972	1055	83
Peat + sand 50 + 50	605	750	55
Peat + sand 21.6 + 78.6	450	485	35
Sand 100 %	68	120	52

Table 3

ORP and specific electrical conductivity of the water extract

Sample	Electrical conductivity, $\mu\text{S/cm}$		ORP, mV	
	Check	Treatment	Check	Treatment
Peat 100 %	465	544	+38	+815
Peat + sand 78.6 + 21.4	360	390	+65	+665
Peat + sand 50 + 50	270	340	+72	+94
Peat + sand 21.6 + 78.4	95	166	+81	+98
Sand 100 %	27	44	+94	+105

The strongest influence of the corona discharge treatment was exercised on the indicator of redox conditions. In all samples under check this indicator ranged from +38 mV for pure peat to +94 mV for pure sand. These ORP values means that reducing conditions prevail, which is characteristic from a perspective of the objects' genesis. Peat is a hydromorphic structure, with reduction processes prevailing in its genesis.

The influence of treating the samples with the negative corona discharge on the ORP indicator was very substantial. The oxidation process of organic matter is accelerated due to several factors. The main oxidizing factor is the action of ozone and negative ions, which are formed in the gas phase of air when the corona discharge acts upon the air, thus generating negative ions and ozone in the air.

Experiment Using Positive Corona

Table 4 shows the parameters of the positive corona discharge.

As can be seen from Table 4 the exposure conditions varied significantly. Probably, the measurement results were strongly influenced by the humidity level in the laboratory, or the homogenization (mixing) of the peat and sand mixture was incomplete.

Table 5 provides the results derived from the specific electrical conductivity of the soil paste and ORP of samples treated with the positive corona.

The ORP value for the “peat + sand 21.4 + 78.6 %” variant is higher than that for the “peat + sand 50 + 50 %” variant. However, this is not a measurement error but rather an indicator of incomplete homogenization (mixing) of the peat and sand mixture.

In the case of the positive corona ORP turns out to be significantly lower than in the case of the negative corona. This demonstrates the greater potential of using specifically the negative corona for soil activation.

Table 4

Positive corona discharge parameters

Sample	Average current, μA	Average voltage, kV	Average energy, J
Peat 100%	6.3	4.0	9.1
Peat + sand 78.6 + 21.4 %	3.1	13.0	14.5
Peat + sand 50 + 50 %	76	2.5	68
Peat + sand 21.4 + 78.6 %	216	3.9	303
Sand 100%	12.8	10.4	48

Table 5

ORP of the soil paste and specific electrical conductivity of samples treated with the positive corona

Sample	ORP, mV	EC of water extract, $\mu\text{S}/\text{cm}$	EC of paste, $\mu\text{S}/\text{cm}$
Peat 100%	+156	1195	1698
Peat + sand 78.6 + 21.4 %	+110	893	1336
Peat + sand 50 + 50 %	+70	574	923
Peat + sand 21.4 + 78.6 %	+105	282	622
Sand 100%	+45	75	136

Conclusion

Treatment of soil with the corona discharge resulted in a significant influence on the redox potential indicator, which is a positive factor in analyzing the discharge's impact on soil. In all samples under check this indicator ranged from +38 mV for pure peat to +94 mV for pure sand. These ORP values mean that reduction conditions prevail. Peat is a hydromorphic structure, with reduction processes prevailing in its genesis. The influence on the ORP indicator proved

to be very substantial because the oxidation process of organic matter is accelerated by several factors implemented in the corona discharge plasma.

A comparison of the effectiveness of positive and negative coronas shows the higher efficiency of the negative corona. This may be due to the generation of negative ions [10] of O^- and O_2^- , which cause generation of additional atomic oxygen followed by ozone formation. Such a channel is absent when a positive corona acts on air.

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