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OXIDIZED AND REDUCED FORMS OF IRON IN ALLUVIAL SOILS OF FLOODPLAINS OF RIVERS OF THE SIVERSKY DONETS BASIN

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Abstract

Alluvial soils form within the river floodplains. The conditions of soil formation for alluvial soils determines by the specifics of the ratio of biological and geological circulation of substances, rapid development of vegetation, and high biogenicity. They differ significantly from the soils of watersheds in their properties, genesis and use. Iron is requires careful study as one of the chemical elements that are necessary for the life of the biota and as one of the elements that determine the properties of soil. Iron, as a chemical element with variable valence, is in oxidized and reduced forms in soil. Their determination carries out in an acidic extract using α-α-dipyridyl by the colorimetric method. The results indicate that there is a connection with the iron content of the soil located on the floodplain, with the depth.

***Key words**: floodplain, alluvial soil, oxidized and reduced forms of iron.*

INTRODUCTION

Among the diversity of the world's landscapes, a special place occupies by floodplains, which distinguishes by their youth and vulnerability among parts of the river valley. In this area in the modern period, there are complex processes of formation and development of many components of the landscape, including soils (Cipriano-Silva, et al., 2020). Floodplain alluvial soils differ significantly from watershed soils both in their genesis and properties, ecological significance, and in use. The main factors of alluvial soil formation are the influence of floods, shallow groundwater, features of sedimentogenesis and constant introduction of material from the above areas. These soils characterize by dynamic of soil processes and complex biocoenotic structure (Bullinger-Weber G. & Gobat J.-M., 2006).

Alluvial soils (fluvisols) in the world occupy a relatively small area – 320 million hectares (Arnold R.W., Szabolcs I., & Targulian V.O., 1990). In Ukraine, their area is 1.4 million hectares, which is insignificant compared to the area of prevalent soils, especially chernozems. These soils make up the main fund of pastures and hayfields, which is due to the presence in this area of highly productive mesohygrophytic and hygrophytic cereal – motley grass meadows (Hikmatullah & Al-Jabri M., 2007). To support the functioning of the soil-plant system, it is necessary to study the ecological condition of floodplain soils. One of the indicators for assessing the ecological condition of soils is data on the content and dynamics of chemical elements. Because they are available for root uptake by plants and are actively involved in the biochemical cycle (Breemen N., 1988). In addition, studies in this area are great scientific value for studying the genesis and evolution of alluvial soils.

Iron, as one of the chemical elements, plays an important role both in soil genesis and in the processes of plant life (Breemen N., 1988).

Iron is one of the most abundant elements in nature. Clarke Fe in Earth's crust, according to Taylor S. R. (Taylor S.R., 1964), is 5.6%. Clarke Fe in soil is 3.8% (Chertko N.K. & Chertko E.N., 2008). Iron in the soil forms its own minerals, and is a part of silicates, sulfides, phosphates, arsenates and iron-organic complexes (Irmak S., Surucu A.K., & Aydin S., 2008).

Iron-containing minerals determine the color of soils, and the patterns of their transformation and content are used in the description of soil processes and soil classification to a large extent. Iron is involved in almost all elementary soil-forming processes: metamorphism of the mineral and organic matter of the soil, migration, segregation and cementation of substances in the soil, podzolization, gleying, etc. (Villalobos & Tebo, 2005).

The character of its distribution along the profile of alluvial soils, which forme in a complex biogeochemical setting, is also of interest in addition to the iron content. The specificity of the distribution of this chemical element along the soil profile is associated with the unequal duration of the processes of saturation of the horizons with water both by the river water and by the soil water itself, the peculiarity of the species composition of plants, physic-chemical properties, and different granulometric and mineralogical compositions of alluvium (Barron & Torrent, 2013).

The issue of the content and distribution of iron in soils for floodplain alluvial soils of the Siversky Donets river basin insufficiently studied by our point of view.

The aim of our study was to study the content and profile distribution of Fe (II) and Fe (III) in the floodplain alluvial soils (fluvisols) of the Siversky Donets river basin in different parts of the floodplain territory.

MATERIALS AND METHODS

The studies were carried out within the following territories: the riverbed part of the Olkhovatka river floodplain, Kharkov district, Kharkov region (Figure 1), the central part of the Merla river floodplain, Bogodukhovsky district, Kharkov region (Figure 2), riverbed, central and near-terrace parts of the Siversky Donets river floodplain, Chuguevsky district, Kharkov region (Figure 3).

The soil cover of the floodplains of the rivers of the Siversky Donets basin on the territory of the Kharkov region of Ukraine is diverse. On the territory of the riverbed part of the Olkhovatka river floodplain, Kharkiv district, Kharkiv region, the following alluvial soils studied: Gleyic Fluvisol (N 49.775989°, E 35.936633°), Humi-Gleyic Fluvisol (N 49.771711°, E 35.934696°), Gleyic-Histic Fluvisol (N 49.771267082°, E 35.933323°).

On the territory of the central part of the floodplain of the Merla river, Bogodukhovsky district, Kharkov region, the following alluvial soils were studied: Gleyic Fluvisol (N 50.02082°, E 35.08576°), Gleyic Fluvisol (N 50.01830°, E 35.08676°), Calcari-Gleyic Fluvisol (N 50.03927°, E 35.14388°).

Figure 1. General view of Olkhovatka river floodplain

Figure 2. General view of Merla river floodplain

Figure 3. General view of Siversky Donets river floodplain

On the territory of the near-channel part of the floodplain of the Siversky Donets River Gleyic Fluvisol (N 49.750826°, E 36.545599°) studied.

On the territory of the central part of the floodplain of the Siversky Donets river Calcari-Gleyic Fluvisol (N 49.752337°, E 36.554064°) studied.

On the territory of the near-terrace part of the floodplain of the Siversky Donets River Humi-Gleyic Fluvisol (N 49.751103°, E 36.551698°) studied.
Mesophilic and hygrophilic herbaceous vegetation grew on the territory of the floodplains. The territories used as natural hayfields and pastures.
Soil samples take from each horizon in the summer. Soil samples of natural moisture poured in field conditions with 0.1 N H_2SO_4 solution in the ratio of 1 part of soil to 10 parts of acid.
Method for determining chemical parameters. Determination of iron oxides in an acidic extract carried out using α-α-dipyridyl by the colorimetric method. Fe (II) and Fe (III) were determined simultaneously in two portions from the same acid extract. In the first portion, Fe (II) was determined, in the second, the sum of Fe (II) and Fe (III), having previously converted Fe (III) into Fe (II) with hydroxylamine. The Fe (III) content is determined as the difference between the sum of Fe (II) and Fe (III) and the value of Fe (II), multiplying the resulting difference by a factor of 1.11.

RESULTS AND DISCUSSIONS

Three research sites were established within the near-channel part of the Olkhovatka River floodplain. The following soils were described on them: Gleyic Fluvisol, Humi-Gleyic Fluvisol, Gleyic-Histic Fluvisol.
The amount of reduced iron forms decreases with increasing depth in the Gleyic Fluvisol of the near-channel part of the Olkhovatka River floodplain. The soil profile for this indicator can be divided into two parts. The first is to a depth of 57 cm, which includes layers of 0-35 and 35-57 cm, where the content of the described forms of iron is slightly more than 2 mg/kg of soil. The second part – from a depth of 57 cm to 105 cm, which also includes two layers -57-70 and 70-105 cm. Here the amount of reduced forms of iron is less than 2 mg/kg of soil (Table 1).
The amount of oxidized forms of iron prevails over the reduced ones by 3-18 times, and is equal to 35.00-5.35 mg/kg of soil. Their number decreases with depth along the profile. The amount of oxidized forms of iron at a depth of 35-57 cm is greater than in the upper layer of 0-35 cm by 0.9 mg/kg of soil. The amount of this form of iron decreases deeper than 57 cm, especially in the layer 75-105 cm to 5.35 mg/kg of soil.

Table 1 Content and profile distribution of oxidized and reduced forms of iron in alluvial soils of the Olkhovatka river floodplain

Soil name	Depth, cm	Content of oxidized and reduced forms of iron, mg/kg soils	
		Fe (II)	Fe (III)
Gleyic Fluvisol	0-35	2.34	35.00
	35-57	2.06	35.90
	57-70	1.79	23.81
	70-105	1.60	5.35
Humi-Gleyic Fluvisol	0-35	2.23	36.97
	35-43	1.30	13.20
	43-70	3.50	58.50
	70-90	1.98	25.62
Gleyic-Histic Fluvisol	0-10	3.38	34.02
	10-25	3.63	24.20
	25-40	4.07	21.03
	40-105	9.91	33.30
	105-125	12.10	8.00

The content of reduced forms of iron in Humi-Gleyic Fluvisol unevenly distributed with increasing depth. Its smallest is in the 35-43 cm layer - 1.30 mg/kg of soil. The maximum value was recorded in the next layer of soil - 43-70 cm - 3.50 mg/kg of soil. The amount of this form of iron is 36% less from the maximum value in the upper layer to a depth of 35 cm. The amount of Fe (II) compounds is 1.5 times greater than the minimum value and amounts to 1.98 mg/kg of soil in the deepest layer, which was studied.
The amount of oxidized forms of iron prevails over the reduced forms, as in the previous soil. The tendency of distribution over layers with depth remains. Fluctuations in the content of oxidized forms of iron has varied between 58.50-13.20 mg/kg of soil. Their maximum founded at a depth of 43-70 cm, and a minimum - at a depth of 35-43 cm. The greatest difference between the depths in the content of oxidized forms of iron is 45.3 mg/kg of soil.
There is a clear tendency towards an increase in the content of reduced forms of iron with depth at the Gleyic-Histic Fluvisol of the riverbed floodplain of the Olkhovatka River. Their

number increases evenly by an average of 0.3-0.4 mg/kg of soil to a depth of 40 cm. The content of these forms of iron increases sharply deeper than 40 cm. The difference in content between the layers is 3-5 mg/kg of soil.

The content of oxidized forms of iron is much higher than that of reduced iron. The amount of oxidized iron tends to decrease with increasing depth. The maximum values of the content of these forms are confined to the depths of 0-10 and 40-105 cm is 34.02 and 33.30 mg/kg of soil. This form of iron is approximately 10 mg/kg of soil less in the layers of 10-25 and 25-40 cm. The amount of iron drops sharply to 8.00 mg/kg of soil in the lower soil layer with a depth of 105-125 cm.

The amount of reduced forms of iron with depth varies between 1.58-0.88 mg/kg of soil in the Gleyc Fluvisol of the central floodplain of the Merla River and decreases with depth. The amount of reducing forms of iron in the upper horizon 0-20 cm compare to its content in the lower layer. The amount of Fe (II) compounds decreases significantly deeper than 50 cm to 0.88 mg/kg of soil in the layer of 120-130 cm. Almost the same amount of these compounds in the soil layers of 50-70 cm and 70-100 cm is observed (Table 2).

Table 2 Content and profile distribution of oxidized and reduced forms of iron in alluvial soils of the Merla river floodplain

Soil name	Depth, cm	Content of oxidized and reduced forms of iron, mg/kg soils	
		Fe (II)	Fe (III)
Gleyic Fluvisol	0-20	1.44	20.45
	20-50	1.58	30.17
	50-70	0.98	14.34
	70-100	1.00	12.28
	120-130	0.88	10.90
Gleyic Fluvisol	0-22	1.41	23.85
	22-55	2.51	21.29
	55-70	2.39	24.55
Calcari-Gleyic Fluvisol	0-22	2.55	18.97
	22-52	1.59	18.08
	52-65	1.76	13.57
	65-110	0.74	6.47
	110-130	0.14	0.75

The number of oxidized forms of iron significantly exceeds the number of reduced forms at all depths. The maximum content of oxidized forms at a depth of 20-50 cm is 30.17 mg/kg of soil. The number of these forms of iron is one and a half times less in the upper sphere of 0-20 cm is 20.45 mg/kg of soil. The amount of this form of iron from 50 cm and deeper gradually decreases and reaches a minimum value, which is three times less than the maximum, - 10.90 mg/kg of soil.

The trend towards a decrease the amount of reduced iron forms in the Gleyic Fluvisol of the central floodplain of the Merla River does not persist with depth. The maximum amount of these forms of iron is at the middle part of the profile at a depth of 22-55 cm is 2.51 mg/kg of soil. The amount of the reduced form of iron decreases by 1.1 mg/kg of soil compared to the maximum value for a horizon with a depth of 0-22 cm. Their amount decreases only by 0.14 mg/kg of soil in a horizon with a depth of 55-70 cm.

The oxidized forms of iron in this soil are, on average, 10 times more than the reduced ones. The distribution of their number with depth has the form of a curve with minimum values in the middle part of the profile and maximum values in the upper and lower horizons.

The maximum content of reduced iron forms in the upper part of the profile of the Calcari-Gleyic Fluvisol of the central floodplain of the Merla River exists up to a depth of 65 cm. The fluctuation of their amount occurs within the range from 1.76 mg/kg of soil to 2.55 mg/kg of soil with the highest value in the soil layer 0-22 cm. The content of reduced forms of iron from 65 cm and deeper sharply decreases to 0.74-0.14 mg/kg of soil.

The content of oxidized forms of iron in comparison with the reduced forms in the Calcari-Gleyic Fluvisol increases by 7-11 times with increasing depth. With increasing depth, the amount of Fe (III) decreases. The difference in the content of this form of iron between the upper layer and the lower one is more than 25 times (layer 0-22 cm - 18.97 mg/kg of soil, layer 110-130 cm - 0.75 mg/kg of soil). The amount of oxidized forms of iron changes little from the surface to a depth of 52 cm. Deeper changes in the content are more pronounced. In a layer with a depth of 52-65 cm, their number decreases by about 5 mg/kg of soil. In the 65-110 cm layer - more than twice, and in the 110-130 cm layer - more than eight times.

The amount of reduced forms of iron in the Gleyic Fluvisol of the near-channel part of the floodplain of the Siversky Donets River range from 1.70 mg/kg soil to 0.26 mg/kg soil. The peak in the content of these forms of iron at a depth of 27-50 cm is 1.70 mg/kg of soil. Deeper, their number decreases by more than four times and corresponds to the value of 0.30-0.26 mg/kg of soil. The number of reduced forms of iron above 27 cm also decreases in comparison with the maximum value is not so critical. The decrease is only 0.39-0.41 mg/kg soil (Table 3).

Table 3 Content and profile distribution of oxidized and reduced forms of iron in alluvial soils of the Siversky Donets river floodplain

Soil name	Depth, cm	Content of oxidized and reduced forms of iron, mg/kg soils	
		Fe (II)	Fe (III)
Gleyic Fluvisol	0-10	1.29	2.26
	10-27	1.31	1.37
	27-50	1.70	1.77
	50-77	0.30	0.81
	77-95	0.26	0.44
Calcari-Gleyic Fluvisol	0-8	1.75	3.25
	8-55	1.13	1.88
	55-65	1.04	1.26
	65-83	0.48	0.55
	83-105	0.24	0.35
Humi-Gleyic Fluvisol	0-8	1.32	3.65
	8-22	0.64	2.31
	22-42	0.86	2.27
	42-55	0.41	0.57
	55-76	0.28	0.34
	76-114	0.19	0.23

The amount of oxidized iron decreases with depth. The range in which the content of these forms of iron fluctuates is 2.26-0.44 mg/kg of soil. The content of Fe (III) compounds slightly increases at a depth of 27-50 cm in comparison with the topsoil.

The content of Fe (II) compounds in the Calcari-Gleyic Fluvisol of the central part of the floodplain of the Siversky Donets River averages 0.93 mg/kg of soil. The maximum amount of this form of iron exists in the upper soil layer 0-8 cm - 1.75 mg/kg of soil. The minimum - in the layer 83-105 cm - 0.24 mg/kg of soil. The decrease in the amount of reduced forms of iron occurs gradually to a depth of 65 cm, and deeper, the decrease has a sharp character, where the amount of iron forms decreases by more than 50%.

There are slightly more oxidized forms of iron in this soil. Their number does not exceed 3.25 mg/kg of soil and does not go below 0.35 mg/kg of soil. There are two sharp decreases in the content of these forms of iron along the soil profile. The first one is at a depth of 8-55 cm, where the indicator decreases by 1.37 mg/kg of soil. The second is at a depth of 65-83 cm is a decrease of 0.71 mg/kg of soil.

The amount of reduced forms of iron in the Humi-Gleyic Fluvisol of the near-terrace depression decreases with depth. The difference in terms of the content of reduced forms of iron between the layers is approximately 55%. An exception to this trend is the soil layer 22-42 cm, where the content of Fe (II) forms, on the contrary, increases to 0.86 mg/kg. Deeper, the downward trend in iron content persists. The total range of values for the content of these forms of iron is 1.32-0.19 mg/kg soil.

The number of oxidized forms of iron is 1.5-2 times higher than that of reduced iron, which is 3.65-0.23 mg/kg of soil. The amount of this form of iron with depth reduce by more than ten times. It is possible to distinguish two soil layers with a depth of 8-22 and 22-42 cm, where the amount of oxidized forms of iron varies little with depth.

CONCLUSIONS

The content of oxidized forms of iron in all studied alluvial soils is higher than the content of reduced forms of iron and is independent of the granulometric composition of the soil and its occurrence in parts of the floodplain.

According to the decrease in the content of iron forms, one can make the following series: alluvial soils of the floodplain of the Olkhovatka River - alluvial soils of the floodplain of the Merla River - alluvial soils of the floodplain of the Siversky Donets River.

According to the averaged data, the largest amount of iron founds in the soils of the riverbed part of the floodplains.

The smallest amount of iron is in Calcari-Gleyic Fluvisol.

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