Scientific Papers. Series A. Agronomy, Vol. LXVII, No. 2, 2024
ISSN 2285-5785; ISSN CD-ROM 2285-5793; ISSN Online 2285-5807; ISSN-L 2285-5785

THE ROLE OF IRON COMPOUNDS IN THE FORMATION OF THE FERTILITY OF HYDROMORPHIC SOILS OF THE FLOODPLAINS OF THE LEFT BANK FOREST STEPPE OF UKRAINE

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Abstract

The special role of iron compounds in the formation of the fertility of alluvial Fluvisols is an actual direction of research. The purpose of the work is to establish the laws of transformation, migration and accumulation of iron in floodplain soils, taking into account the peculiarities of the conditions of their formation and the influence of these processes on their fertility. These processes have an important genetic-diagnostic and agro-ecological role. The regularities of the content and profile distribution of non-silicate forms of iron in floodplain soils of the Left Bank Forest-Steppe of Ukraine with different degrees of hydromorphism are indicated in the article. Iron significantly affects the content of nutrients in plants, in particular, the content of phosphorus and potassium. Fixing them in a form inaccessible to plants can cause a deficiency in mineral nutrition of plants. The transformation of organic matter occurs with an increase in the content of the fulvic acid group under conditions of waterlogging. There is a sharp increase in the solubility of iron hydroxide at the same time. Collectively, all this leads to the migration of iron compounds along the soil profile and the formation under certain conditions of concretionary forms of iron that can impair soil fertility. The introduction of different doses of iron did not significantly affect the acid-alkaline balance of the soil solution. The pH remained within the neutral range.

Key words: *floodplain, alluvial soils, iron.*

INTRODUCTION

Floodplain soils are found in all natural zones of Ukraine. The area of floodplain soils within agricultural lands is 5.3 hectares.

The pH of the soils of the floodplains of the small rivers of the Left Bank of the Forest Steppe is neutral or close to alkaline. They are layered, glazed, enriched with nutrients. The soils of the floodplains of small rivers of the Livoberezhny Forest Steppe were formed under the action of the humus-accumulative process. A characteristic feature of all types of floodplain soils is hydromorphism, expressed to one degree or another. The high fertility potential of these soils is due to their special function of a kind of trap (barrier, filter) on the way of migration and accumulation of many substances and elements in nature. Among them are such important biogens for plants as iron, calcium, nitrogen, phosphorus, etc. In the spring, flood waters bring various water-soluble and suspended mineral particles into the floodplain, which enrich the soil cover of the floodplain.

Under conditions of stagnation, introduced oxidizing compounds of iron are restored and turn into active forms of oxidized iron. The latter significantly affect the state of potential fertility, which is reflected in the productivity of meadow phytocenoses. Groundwater also becomes a source of iron supply to floodplain soils. In the absence of dissolved oxygen in groundwater, it is usually found in the form of soluble compounds with Fe^{2+} ions.

With the appearance of mobile forms of iron in the soil, the accumulation of iron phosphates, which are poorly soluble and scarcely available compounds for plant nutrition, can be traced (Truskavetskyi et al., 2020; Ginsburg, 1981; Truskavetskyi & Zubkovska, 2015). In the work of prominent scientists indicates the priority role of one and a half oxides in the absorption of phosphates. This is particularly evident in floodplain soils.

Iron is a necessary and irreplaceable element of mineral nutrition and an active regulator of oxidation-reduction (OR) processes in the soil. Recovery of iron occurs at Eh from +100 to -

600 Mv. In hydromorphic soils, under oxidizing conditions, recovery processes can occur, with a local reduction of ORP to 300-350 mV and below. In such cases, both forms of iron are constantly or periodically present in the soil, or divalent forms predominate.

It is worth noting that the solubility of iron compounds is affected by the pH of the medium. In a strongly acidic environment, the mobility of iron hydroxide increases and iron ions appear in the soil solution. In soils with a neutral or alkaline reaction (pH >7), its solubility is usually reduced, which can lead to the formation of insoluble forms of iron and reduce its availability to plants.

The content of organic matter plays an important role in soil fertility. In floodplain soils, a significant role in the fixation of humic substances is played by oxides and a half, in particular free compounds of iron, which are able to form strong iron-organic complexes with fulvic acids under a dynamic redox regime.

Various properties of iron determine the interest of researchers in it as a diagnostic indicator of many macro- and micro-processes of soil formation and as a factor in the fertility of floodplain soils (Zaidelman, 2017; Zonn, 1982; Qiu et al., 2016; Li et al., 2018; Khan et al., 2015).

Taking into account the active participation of iron in many soil processes and the insufficient study of this issue, there is a need for additional research on its role in the formation of floodplain soil fertility.

The purpose of our research was to determine the content of mobile forms of iron, the dynamics of redox conditions, the nature of the water-air regime, the level of acid-base balance and phosphate mode in the floodplain soils of the Left Bank Forest Steppe of Ukraine and the influence of these factors on their fertility.

MATERIALS AND METHODS

The research was conducted during the growing season at the sites of the stationary experiment on the Humi-Gleyic Fluvisol (N 49°46'16.6", E 35°55'60.0") drained by a network of open channels and Calcari-Gleyic Fluvisol (N 49°46'33.6", E 35°56'11.9") in the floodplain of the Vilkhovatka River (Kharkiv District, Kharkiv Region) (Figure 1). Soil samples were taken three times in different periods: spring, summer and autumn.

Figure 1. Aerial view of the floodplain of the Vilkhovatka River

In order to preserve oxidized forms of iron and prevent their oxidation, the analysis was carried out in soil samples preserved with toluene, which were urgently sent to the laboratory for determination of oxidized and oxidized forms of iron. Soil samples were filled with 1N H_2SO_4 solution in the ratio of 1 part of soil to 10 parts of acid.

Determination of iron oxides in the acid extract is carried out using o-phenanthroline by colorimetric method. Fe^{2+} and Fe^{3+} were determined simultaneously in two portions from the same acid extract. In the first portion, Fe^{2+} was determined, in the second, the sum of Fe^{2+} and Fe^{3+} was previously converted into Fe^{2+} with hydroxylamine. The content of Fe^{3+} is determined as the difference between the content of Fe^{2+} and Fe^{3+} and the value of Fe^{2+} multiplied by a factor of 1.11.

The redox potential was measured in the field using a portable pH-meter-millivoltmeter I-130 in the walls. The EMF was measured (in mV) between the EPV-1 thin-layer platinum electrode and the EVL-1M auxiliary silver chloride electrode, which were lowered into the soil ball, to determine the soil redox potential. The determinations were accompanied by the measurement of the following parameters: humidity, temperature, and soil acidity (pH).

In the version with fertilizers, ammonium nitrate was used as nitrogen fertilizers at the rate of 120 kg/ha based on the active substance. Simple

superphosphate and potassium salt were also applied at the rate of 50 kg/ha per active substance.
Determination of the effect of iron on the phosphate function was carried out in a model experiment on the example of Calcari-Gleyic Fluvisol medium-loamy (content of particles < 0.01 mm - 38.61%) alluvial soil. The soil is low in humus (3.12%) with pH_{H_2O} 7.5. The experiment consists of two blocks with four options in each. The first block is carried out with optimal humidity (70% of the full moisture content). The second unit was artificially overmoistened (up to 90% of full moisture content). The background of both blocks contained complete organo-mineral fertilizer $N_{60}P_{120}K_{60}$+decomposed manure.
Iron hydroxide was added to these backgrounds in all blocks in the following versions with increasing doses of loads (400, 800 and 1600 mg/kg of soil). The study was carried out in 3 repetitions in containers containing 0.6 kg of soil each. The test culture is Badyory barley.
The determination of mobile phosphorus compounds was performed according to the modified Machigin method: extraction of mobile phosphorus compounds from the soil was carried out with a 1% solution of ammonium carbonate ($(NH_4)_2CO_3$) (pH 9.0) at a soil-solution ratio of 1:20 and a temperature of 25 ± 2°C. Phosphorus is determined photocolorimetrically by the color intensity of the phosphorus-molybdenum complex.

RESULTS AND DISCUSSIONS

The redox regime of the soil is closely related to water and thermal regimes. The highest value of field soil moisture is observed in the spring period (Table 1), when the soil is saturated with flood and melt water. In summer, it decreases by 1.4-5.3 times due to an increase in air temperature and increased transpiration, and in autumn it increases slightly due to precipitation. The surface 0-20 cm horizon remains the least moistened. Humidity increases in glaciated horizons as it approaches the level of groundwater. In May of the first year of research, the groundwater level was at a depth of 60-80 cm, already in August - 100-150 cm, and in October 80-100 cm.

Table 1. Dynamics of ORP, pH and moisture content in drained Humi-Gleyic Fluvisol

Version	Depth, cm	Spring			Summer			Autumn		
		pH	Eh, mV	moisture content, %	pH	Eh, mV	moisture content, %	pH	Eh, mV	moisture content, %
2009										
Control	0-20	7.2	498	20.2	7.1	528	4.6	7.1	512	4.9
	20-50	7.0	451	23.1	7.1	532	6.6	7.1	522	6.5
	50-65	6.8	447	39.4	6.8	489	7.4	6.9	478	8.7
$N_{120}P_{50}K_{50}$	0-20	7.0	505	20.7	6.8	494	4.2	6.9	504	6.7
	20-50	6.9	523	30.1	6.8	500	10.4	6.9	497	5.6
	50-65	6.8	456	45.5	6.7	472	32.0	6.8	468	15.3
2010										
Control	0-20	7.0	476	16.1	7.2	571	10.2	7.1	537	28.6
	20-50	6.8	506	21.0	7.0	506	13.9	7.1	552	29.2
	50-65	6.8	501	45.1	6.8	436	17.7	6.9	529	35.4
$N_{120}P_{50}K_{50}$	0-20	6.8	496	21.3	6.7	467	8.9	6.7	534	31.8
	20-50	6.9	503	22.8	6.7	474	16.1	6.7	510	27.4
	50-65	6.8	432	53.2	6.8	492	26.2	6.7	492	41.0
2011										
Control	0-20	7.0	524	25.2	7.0	518	10.8	7.1	482	12.3
	20-50	6.8	543	27.9	6.9	520	10.0	6.9	443	13.8
	50-65	6.9	561	30.3	6.8	504	12.3	6.8	445	24.2
$N_{120}P_{50}K_{50}$	0-20	6.8	539	29.3	6.8	523	15.1	6.8	509	15.3
	20-50	7.0	565	32.1	7.0	517	14.0	6.9	477	14.8
	50-65	6.9	586	43.2	6.9	506	18.9	7.0	490	25.5

Measurements of the soil temperature in the surface layer at a depth of 5-10 cm showed that the greatest warming of the soil, on average, to +18°C, occurs in summer, and the least in autumn, around +5°C, while in the spring the temperature was at the level of +8°C.
When the temperature rises in the spring-summer period, the humus horizons of the investigated hydromorphic soils dry out and are enriched with oxygen due to the establishment

of oxidizing conditions during this period. At the same time, thanks to the presence of organic substances, which floodplain soils are rich in, the activity of microflora, which also requires oxygen, is activated.

The introduction of mineral fertilizers in doses of $N_{120}P_{50}K_{50}$ affects the indicator of oxidation-relative potential, if a gradual decrease in the Eh indicator is observed on the option of control over the sampling depths of soil samples (0-20, 20-50 and 50-65 cm), then the introduction of mineral fertilizers violates this regularity. For example, in the spring of 2009, during the control, the ORP index decreases layer by layer in the following order: 498, 451, and 447 mV, then when mineral fertilizers are applied in the same soil layers, this indicator is slightly higher, respectively 505, 523, and 456 mV. That is, in our opinion, it is obvious the fact that the introduction of mineral fertilizers increases the Eh indicator can be traced.

Certain redox conditions are necessary for the better development of meadow phytocenoses. Seasonal dynamics of ORP on the control variant increases in summer and autumn. The maximum value of Eh was determined at the level of 571-537 mV, which was recorded in the second year of research. Meadow grasses do not show any noticeable signs of suppression at such values of the ORP indicator. In the lower horizons, the indicator of redox potential decreases. Restorative processes can develop in separate zones. But they do not determine the general orientation of redox conditions both along the genetic horizons and over the entire soil profile.

It should be especially noted the developed microzonal redox reactions in peated layers at a depth of 50-65 cm in summer with a high content of mobile forms of iron and a decrease in pH during this period (Table 2). And although in the real soil and ecological situation there is no direct proportional relationship between the value of ORP and the content of mobile compounds of oxidized and oxidized iron, still sometimes, due to the decrease of ORP in the lower horizons of floodplain soils, a partial reduction of iron is also observed. We recorded these patterns in the 50-65 cm soil layer in the spring of the first year of research.

Table 2. The dynamics of the content of mobile oxidized and oxidized iron compounds in the Humi-Gleyic Fluvisol of the Vilkhovatka river floodplain

Version	Depth, cm	Content of acid-soluble iron, mg/kg of soil								
		Spring			Summer			Autumn		
		FeO	Fe_2O_3	∑	FeO	Fe_2O_3	∑	FeO	Fe_2O_3	∑
2009										
Control	0-20	353	2092	2445	296	2327	2623	185	2762	2947
	20-50	366	2146	2512	271	2576	2847	248	2713	2961
	50-65	813	1441	2254	196	2703	2899	434	2819	3253
$N_{120}P_{50}K_{50}$	0-20	214	2052	2266	145	2243	2388	189	2224	2413
	20-50	227	2236	2463	242	2709	2951	257	2540	2797
	50-65	691	1923	2614	573	2413	2986	604	2439	3043
2010										
Control	0-20	252	1994	2246	161	2373	2534	121	2591	2713
	20-50	396	2276	2672	361	2560	2921	221	2785	3002
	50-65	703	1673	2376	276	2823	3104	300	3056	3357
$N_{120}P_{50}K_{50}$	0-20	136	2285	2421	186	2858	3044	166	2082	3658
	20-50	506	1918	2424	442	2736	3178	313	3345	3658
	50-65	927	2973	3900	578	4426	5004	922	4037	4953
2011										
Control	0-20	302	2239	2541	154	2666	2820	167	3190	3357
	20-50	418	2356	2774	221	2921	3142	376	3517	3893
	50-65	871	1448	2319	301	2698	2999	476	3596	4072
$N_{120}P_{50}K_{50}$	0-20	172	1828	2000	175	2336	2511	123	2268	2391
	20-50	559	2354	2913	276	3260	3536	398	2780	3178
	50-65	914	1932	2846	585	5496	6081	1069	5480	6549

In the seasonal dynamics, an increase in the total content of mobile iron compounds was characteristic in the warm summer months, when favorable conditions are created for the mobilization of its potential reserves, the value of this indicator in the soil layer 0-20 cm in the control was 2623 mg/kg, in the lower horizon 20-50 cm it was equal to 2847 mg/kg, and for

50-65 depth it was at the level of 2899 mg/kg. In the autumn, the total content of mobile iron compounds in the meadow-swamp soil increases significantly compared to the summer period, in all horizons, both in the control and in the fertilized version.

Thus, in the spring of the second year of research, the content of total mobile iron did not exceed 2246 mg/kg of soil in the near-surface layer of the control variant, which is explained by a decrease in biological activity during this period. Moisture reserves in the period of summer measurements significantly decreased in all genetic horizons. Under such conditions, a redox environment is created, which prevents the formation of oxidized forms and stabilizes elements of variable valency, in particular iron.

Taking into account the fact that soil moisture actively affects its air, thermal, nutritional regimes, it is possible to draw a conclusion about the mandatory need to monitor its optimal regulation throughout the growing season.

Studies of the dynamics and profile distribution of oxidized and oxidized iron in the alluvial meadow-swamp soil showed that the content of oxidized iron is significantly higher than that of oxidized iron Fe^{2+} in the unfertilized control within the entire soil profile. When the air temperature increases and soil aeration improves in the summer, the amount of oxidized iron decreases and the amount of oxidized iron increases, which is well monitored by the Fe^{2+}/Fe^{3+} ratio.

The content of oxidized forms increases noticeably with depth. The increased content of oxidized iron at a depth of 50-65 cm is facilitated by the presence of a well-decomposed peat layer, as well as the elevation of the capillary border to this horizon and the deposition of mobile iron compounds on the border of the contrast of changes in redox conditions. This regularity can be traced both in the control and in the fertilized version of the field experiment.

The profile heterogeneity of the content of acid-soluble forms of iron, which is clearly visible in the studied soil, is caused, first of all, by the contrast of ORP, as well as the granulometric and mineralogical composition of the genetic horizons of the Fluvisol.

According to the granulometric composition, the studied Fluvisol is light loam (the content of physical clay (< 0.01 mm) in the 0-20 cm layer is 29%). The content of humus in the upper horizon is 5.5%. The soil profile has a distinct stratification, which creates conditions for the redistribution of mobile iron compounds and the formation of its accumulation sites. Up to a depth of 65 cm, the soil has a high ORP throughout the growing season (431-571 mV).

The research carried out in 2017-2020 on meadow-swamp light loam drained soil established a decrease in the level of groundwater, which was established respectively at a depth of 90-100 cm in spring, 120-165 cm in summer and 100-120 cm in autumn. Which is on average 20 cm more than in previous years of research. Such changes, in our opinion, are probably related to modern climatic fluctuations due to climate change.

Thus, the changes that have occurred in the temporal dimension (over the past 12 years) may indicate the influence of climatic factors (increased average annual air temperatures, fluctuations in the amount of precipitation, increased frequency of abnormal weather phenomena), which is reflected in the water regime of floodplain soils.

Compared to previous years, in 2017, the direction of redox processes was established in the direction of oxidation, which significantly affected the redistribution of mobile forms of iron with a noticeable increase in the content of its oxidized form (Table 3).

Table 3. The content of mobile oxidized and oxidized iron compounds in the Humi-Gleyic Fluvisol of the floodplain of the Vilkhovatka River (2017)

Depth, cm	Content of acid-soluble iron, mg/kg of soil								
	Spring			Summer			Autumn		
	FeO	Fe_2O_3	∑	FeO	Fe_2O_3	∑	FeO	Fe_2O_3	∑
0-20	291	2130	2421	123	2804	2927	118	2702	2820
20-50	387	1848	2235	198	2336	2534	482	5131	5613
50-65	1291	1923	3214	1150	5866	7016	1059	4952	6011

The contrasting mode of wetting of the studied alluvial soil affected the content of oxidized and oxidized forms of iron and indicators of redox potential. Observations of the dynamics of oxidation-reduction processes in the alluvial floodplain during 2009-2020 showed their dynamics in individual years and seasons. Higher values of ORP are typical for the dry year of 2010.

Contrasting changes in the regimes of "overwetting - drying" (oxidation-reduction processes) in temporal and spatial dimensions affect the state and behavior of the main biogenic elements (phosphorus, nitrogen, potassium). Changes in the phosphate regime due to the strengthening of the antagonistic interaction between phosphorus and iron are especially noticeable.

Floodplain soils are usually distinguished by a sufficiently high natural wealth of gross phosphorus with different contents of its mobile forms. This is due to the accumulation of phosphorus in alluvial sediments and residual phosphates in long-term fertilized floodplain soils. Despite the high biogenicity, organophosphates in floodplain virgin soils reach 30-40% of the gross phosphorus content, decreasing during their agricultural use. The main share of phosphates, similarly to zonal soils, consists of mineral compounds of phosphorus, which are salts of orthophosphoric acid and are represented by salts of calcium, sodium, iron, aluminum and other cations. A characteristic feature of phosphate soil compounds is their low solubility and weak dissociation into ions. Phosphate ions are well fixed by the solid phase of the soil and their migration in the soil is very limited.

The water regime is of great importance for the redistribution of phosphates in floodplain soils. It was established that the stronger the overwetting of the soil and the longer it lasts, the more mobile phosphates are contained in the soil. Simultaneously with the accumulation of mobile forms on fertilized soils, the formation of sparingly soluble compounds and gross phosphorus takes place.

Our laboratory model experiments showed that the introduction of iron hydroxide affected the mobility of phosphates (Table 4). When using organo-mineral fertilizers, the phosphorus content is 64 mg/kg of soil in option 1. At the same time, there is a clear trend towards its decrease in options with the introduction of iron - the content drops to 41 mg/kg of soil (option 4). Waterlogging also negatively affects the phosphate regime of soils, the content of mobile phosphorus decreased to 32 mg/kg of soil (option 8). This can be explained by the ability of oxidized iron to form iron phosphates under conditions of overwetting, remove phosphate ions from the soil solution and thereby worsen the phosphate regime of the soil.

Table 4. The effect of iron compounds on the mobility of phosphates and the biomass of barley seedlings (laboratory model experiment)

Research options	The content of mobile forms of iron mg/kg soil		P_2O_5, mg/kg of soil	Green mass, g/vessel
	Fe^{3+}	Fe^{2+}		
Optimal hydration				
1. $N_{60}P_{120}K_{60}$ + decomposed manure – background	5315	88	64	2.49
2. Fe_{400}	5573	138	55	2.08
3. Fe_{800}	5714	165	50	1.93
4. Fe_{1600}	6089	181	41	1.67
Overwetting				
5. background	5224	208	60	2.36
6. Fe_{400}	5469	285	53	1.96
7. Fe_{800}	5705	312	42	1.74
8. Fe_{1600}	5619	459	32	1.67

It should be noted that the additional application of iron, starting with 400 mg/kg of soil, contributed to a decrease in yield in all variants of the experiment, which increased as the dose of applied iron increased, but the greatest decrease in yield - 1.67 g/pot, was obtained at the dose of applied iron iron 1600 mg/kg of soil.

CONCLUSIONS

The redox regime significantly affects the ratio of elements with variable valence in the soil, primarily iron. With the predominance of reduction processes, the solubility of iron increases and conditions are created for its migration. When reductive processes change to oxidizing ones, the segregation of iron hydroxides and the formation of iron neoplasms occurs, which affects soil fertility. The seasonal change of ORP and the hydrothermal regime of the floodplain-swamp soil determines the dynamics of the ratio of the content of oxidized and oxidized forms of iron. With the improvement of hydrothermal conditions and, accordingly, the biogenicity of the soil, the content of mobile forms of iron increases with a decrease in the Fe^{2+}/Fe^{3+} ratio.

Free (non-silicate) acid-soluble forms of iron significantly influence the behavior of phosphorus in floodplain medium loam soil. Waterlogging of meadow soil leads to the transformation of oxidized iron into oxidized, more mobile and active forms. The latter bind phosphate ions and precipitate, thereby reducing their availability to plants.

With the simultaneous application of iron compounds with organic fertilizer (peat) and optimal moistening, the activity of phosphate ions in the soil solution increases significantly, which is associated with the formation of migratory complex organo-phosphate compounds.

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