PROCESSOS DE OXIDAÇÃO-REDUÇÃO EM SOLOS DE AGROCENOSSES DE ARROZ DA REGIÃO DE KUBAN

OXIDATION-REDUCTION PROCESSES IN THE SOILS OF RICE AGROCENOSSES OF THE KUBAN REGION (RUSSIA)

ОКИСЛИТЕЛЬНО-ВОССТАНОВИТЕЛЬНЫЕ ПРОЦЕССЫ В ПОЧВАХ РИСОВЫХ АГРОЦЕНОЗОВ КУБАНИ

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RESUMO

Introdução: Os estudos foram realizados na matriz de irrigação Maryano-Cheburgolsky no distrito de Krasnoarmeisky, no território de Krasnodar. **Objetivo:** Esse trabalho tem como objetivo estudar os processos de oxidação-redução e a atividade dos compostos de ferro em solos prato-chernozem e prato-pantanosos de agrocecoses de arroz da região de Kuban. **Métodos:** Foram coletadas amostras do solo das plantações de arroz e gramíneas perenes, nos quais foram determinados o valor do pH, do potencial redox (Eh, mV), da suscetibilidade magnética ($\chi \times 10^{-3}$ unidades S.I.) e a porcentagem de compostos de ferro ativos (FeO e Fe₂O₃, mg/100 g). **Resultados e Discussão:** Os processos redutores criados nos solos das plantações de arroz ocorridos após as inundações levaram à transformação de compostos pouco solúveis de Fe₂O₃ em formas mais reativas de FeO. As quantidades máximas de FeO e mínimas de Fe₂O₃ foram registradas durante o período em que o valor do Eh era negativo. A redução máxima do ferro em solos prato-chernozem e prato-pantanosos foi alcançada durante a fase de floração do arroz, quando foram registrados, respectivamente, os seguintes valores de Eh, pH e rH₂: Eh = -127, pH = 7.36, rH₂ = 10 e Eh = -152...-167 mV, pH = 6.89-7.10, rH₂ = 9. **Conclusões:** No solo de cultivo permanente de arroz, a dinâmica do Eh e dos compostos de ferro é similar à dos campos de rotação de culturas de arroz. Nos solos não inundados das plantações de arroz sob gramíneas perenes, prevalece o regime oxidativo e a transformação dos compostos de ferro não é manifestada. Os valores mínimos de χ coincidem com o percentual máximo de ferro ferroso nos solos com valores de Eh negativos, o que corresponde à fase de floração do arroz. Os coeficientes de correlação da variável χ com as variáveis Eh, FeO e Fe₂O₃ ficaram nos intervalos de +0,66 a +0,75, de -0,69 a -0,84 e de +0,74 a +0,77, respectivamente. O valor de χ aumenta no solo sob plantações de gramíneas perenes com predominância de processos oxidativos. O coeficiente de correlação entre as variáveis χ e Fe₂O₃ ficou no intervalo de +0,83 a +0,90.

Palavras-chave: solo prato-chernozem, solo prato-pantanso, plantação permanente de arroz, potencial redox, ferro ativo.

ABSTRACT

Background: The studies were carried out on the Maryano-Cheburgolsky irrigation array in the Krasnoarmeisky district of the Krasnodar Territory. **Aim:** This work aims to study the oxidation-reduction processes and activity of iron compounds in meadow-chernozem and meadow-boggy soils of rice agrocecoses of the Kuban region. **Methods:** Soil samples were taken from paddy fields occupied by rice and perennial grasses, in which the pH value, redox potential (Eh, mV), magnetic susceptibility ($\chi \times 10^{-3}$ S.I. units), and the content of active iron compounds (FeO and Fe₂O₃, mg/100 g) were determined. **Results and Discussion:** The reductive processes created in the soils of rice fields after flooding led to the transformation of poorly soluble Fe₂O₃ compounds into more active reaction forms of FeO. The maximum content of FeO and the minimum amount of Fe₂O₃ were recorded during the period of negative Eh values. The maximum reduction of iron in meadow-boggy and meadow-chernozem soils was achieved by the phase of flowering of rice plants at Eh = -127, pH = 7.36 units,

$r_{H_2} = 10$ and $E_h = -152 \dots -167$ mV, $pH = 6.89-7.10$ units, $r_{H_2} = 9$, respectively. **Conclusions:** In the soil of permanent rice cultivation, the dynamics of E_h and iron compounds are similar to the fields of rice crop rotation. In non-flooded soils of rice fields under perennial grasses, the oxidative regime prevails, and the transformation of iron compounds is not expressed. The minimum values of χ coincide with the maximum content of ferrous iron in soils at negative E_h values, which corresponds to the rice flowering phase. Correlation coefficients of χ with E_h , FeO , and Fe_2O_3 equal from +0.66 to +0.75, from -0.69 to -0.84, and from +0.74 to +0.77, respectively. The χ value increases in the soil under crops of perennial grasses with a predominance of oxidative processes. The correlation coefficient between χ and Fe_2O_3 equals from +0.83 to +0.90.

Keywords: meadow-chnozem soil, meadow-boggy soil, permanent rice cultivation, redox potential, active iron.

АННОТАЦИЯ

Введение: Исследования проведены на Марьяно-Чебургольском массиве орошения в Красноармейском районе Краснодарского края. **Цель:** Цель работы – изучить окислительно-восстановительные процессы и подвижность соединений железа в лугово-черноземной и лугово-болотной почвах рисовых агроценозов Кубани. **Методы:** На рисовых чеках, занятых посевом риса и многолетними травами отбирались почвенные образцы, в которых определяли величину pH , окислительно-восстановительный потенциал (E_h), магнитную восприимчивость (χ) и содержание подвижных соединений железа. **Результаты и Обсуждение:** Восстановительные процессы, создающиеся в почвах рисовых полей после затопления, привели к трансформации труднорастворимых соединений Fe_2O_3 в более подвижные реакционные формы FeO . Максимум содержания FeO и минимум количества Fe_2O_3 зафиксировано в период отрицательных значений E_h . Максимальное восстановление железа в лугово-болотной и лугово-черноземной почвах достигалось к фазе цветения растений риса при $E_h = -127$, $pH = 7,36$ ед., $r_{H_2} = 10$ и $E_h = -152 \dots -167$ мВ, $pH = 6,89-7,10$ ед., $r_{H_2} = 9$ соответственно. **Заключение:** В почве бессменного посева риса динамика E_h и соединений железа аналогична полям рисового севооборота. В не затопляемых почвах рисовых полей под многолетними травами преобладает окислительный режим и трансформация соединений железа не выражена. Минимальные значения магнитной восприимчивости совпадают с максимальным содержанием в почве двухвалентных соединений железа при низких величинах E_h , что соответствует фазе цветения растений риса. Коэффициенты корреляции величины χ с E_h , FeO и Fe_2O_3 составляют от +0,66 до +0,75; от -0,69 до -0,84 и от +0,74 до +0,77 соответственно. Величина χ увеличивается в почве под посевами многолетних трав при преобладании окислительных процессов; коэффициент корреляции между χ и Fe_2O_3 составляют от +0,83 до +0,90.

Ключевые слова: лугово-черноземная почва, лугово-болотная почва, бессменный посев риса, окислительно-восстановительный потенциал, подвижное железо.

1. INTRODUCTION:

The cultivation of lowland rice causes fundamental changes in soil-forming processes and the nature of the hydrological situation. During the growing season, the soils are under a water layer, which causes the creation of reductive conditions in them annually for 4-5 months. These conditions are reflected in their morphological and physical, chemical, biochemical, and biological properties (Bahmanyar, 2007; Sheudzhen and Gutorova, 2020; Sheudzhen, Gutorova, Shein, and Romanenkov, 2019; Huang, Thompson, Zhang, Chen, Han, and Gong, 2015).

Iron is a necessary and irreplaceable element of the mineral nutrition of rice plants and an active regulator of oxidation-reduction processes in the soil. The genesis of paddy soils is closely related to the transformation of iron compounds. The periodically occurring reductive

processes in the soil under the rice favor the iron supply of plants. Iron enters the plant in the form of Fe^{2+} and Fe^{3+} cations and the form of chelates (Huang *et al.*, 2015; Chacon, Silver, Dubinsky, and Gusack, 2006; Fageria, Baligar, and Wright, 1990; Shahid *et al.*, 2017; Annisa and Nursyamsi, 2016). The reduction of Fe^{3+} to Fe^{2+} in the soil begins at $pH = 6.0$, and a decrease in the redox potential (E_h) to 220 mV and in conditions of $pH = 7.0$ units and $E_h = 160$ mV (Brümmer, 1974). This favorably affects the supply of rice plants with iron, but under certain conditions, it can also have a negative effect. In a reductive environment at low E_h values around 100-200 mV and below, ferrous iron can precipitate in an ore-like form and result in a form inaccessible to plants (Brümmer, 1974).

An excess of Fe^{2+} content in soil solution can cause toxicosis in rice plants (Li, Kronzucker, and Shi, 2016; Zaid, Ahmad, Jaleel, Wani, and Hasanuzzaman, 2020; Chérif, Audebert, Fofana,

and Zouzou, 2009). In the seedling phase, the root system of rice does not produce enough oxygen. Therefore, the reduced iron in the rhizosphere of the roots is not completely oxidized and partially penetrates the root cells, being oxidized by oxygen intended for the oxidation of intracellular processes. In this case, Fe^{2+} transforms into hydroxide forms, precipitates, and forms drusen in cells and clogs vascular vessels, leading to weakening and even thinning of seedlings (Titkov and Koltsov, 2007). Many studies determine rice yield loss due to excess iron content in the soil (Diedhiou *et al.*, 2020; Sahrawat, 2005; Becker and Asch, 2005; Sahrawat, 2003).

On the other hand, with the accumulation of Fe^{2+} in the soil solution, conditions are created for binding hydrogen sulfide FeS, eliminating the products of anaerobic decomposition, which are toxic to rice. As a result of the reaction described in Equation 1.

sulfurous iron, insoluble in water, is formed. This compound is harmless to rice plants, crystallizing hydrotroilite – $\text{FeS} \cdot n\text{H}_2\text{O}$ (Titkov and Koltsov, 2007).

Iron compounds determine the magnetic properties of the soil, which are most often characterized by the value of magnetic susceptibility (χ). This indicator for different soil types is a physical quantity that characterizes the ability of soil iron-containing minerals to magnetize. Iron minerals, which determine the magnetic susceptibility of soils, are presented as oxides and hydroxides crystallized to varying degrees and differing in the types of crystal lattices (Babanin, Trukhin, Karpachevskii, Ivanov, and Morozov, 1995). In automorphic soils with good aeration and a predominance of oxidizing conditions over reducing iron compounds, ferric oxide and hydroxides accumulate. In hydromorphic soils with a stable waterlogging regime, ferrous iron compounds predominate (Vodyanitskii and Skripnikova, 2000). The value of their magnetic susceptibility depends on the content of iron-containing minerals in soils. The soils of rice fields are dominated by iron-containing oxide and hydroxide minerals such as hematite (Fe_2O_3), goethite ($\alpha\text{-FeOOH}$), lepidocrocite ($\gamma\text{-FeOOH}$), feroxyhyte ($\text{Fe}_3(\text{OH})_8$) (Goton and Patrick, 1973; Akter *et al.*, 2018). Their formation is associated with the dehydration of amorphous hydrated compounds, represented mainly by high molecular weight gels and directly with the destruction of ferruginous minerals

(Zonn, 1982).

In connection with the above, the work aimed to study the oxidation-reduction regime in the soils of rice agroecosystems of the Kuban and the possibility of using the value of magnetic susceptibility as an indicator of its direction.

2. METHODS:

The studies were carried out on the Maryano-Cheburgol irrigation area of the rice irrigation system in the Krasnoarmeisky district of the Krasnodar Territory (45°23'02.77", N; 38°31'06.59", E). The research period lasted from 2016 to 2018.

A temperate continental climate characterizes the natural conditions of soil formation; a large number of positive temperatures above 10 °C, amounting to 3,600 °C; during the growing season of rice plants to 2,920-3,040 °C; low average annual precipitation (589 mm) (K.U. = 0.3-0.4); during the growing season of rice 250-350 mm; inhomogeneous relief (ridge-like near-surface rises, plain spaces and depressions); a small variety of parent rocks, represented by alluvial deposits of various granulometric composition; past growth of meadow-steppe vegetation and a high level of groundwater (1-2 m) (All-Russian Research Institute of Rice, 2005).

Per the geomorphological map of the Krasnodar Territory, the territory of the region belongs to the ancient deltaic accumulative-alluvial plain of the Kuban river. By soil geographical zoning, it belongs to the Azov-Ciscaucasian soil province of the steppe zone of ordinary and southern chernozems and the soil district of the lower reaches of the Kuban river distribution of soils of meadow-steppe and meadow types. The soil cover of the territory is represented mainly by meadow-chernozem (corresponding to Gleyic Chernozem in W.R.B. (IUSS Working Group WRB, 2015)), located on ridges and ridge-like near-river rises of the flooded plains, and meadow-boggy (corresponding to Calcic Chernic Gleysol in W.R.B. (IUSS Working Group WRB, 2015)) soils, formed in closed low regions and depressions. As a result of the construction and operation of the rice irrigation system, the natural relief was disturbed. Its anthropogenic elements are distinguished: low and high paddy fields with absolute marks from +7.2 to +10.7 m.

Within the rice irrigation system, at a short distance from each other, key areas were

selected for sowing rice and perennial grasses:

Plot 1. Meadow-chnozem soil. Sowing rice in the 1st year after a busy fallow (winter wheat).

Plot 2. Meadow-boggy soil. Sowing rice in the 1st year after a busy fallow (winter wheat).

Plot 3. Meadow-chnozem soil. Sowing perennial grasses of the 2nd year.

Plot 4. Meadow-boggy soil. Sowing perennial grasses of the 2nd year.

Plot 5. Meadow-chnozem soil. Permanent rice cultivation for 80 years without fertilization (monoculture since 1937).

Soil samples were taken simultaneously in the central part of rice paddies on counting plots in the arable (0-10 and 11-20 cm) and sub-arable (21-30 and 31-40 cm) soil layers. Samples were taken with a soil drill before the creation of a layer of water above the soil surface and after its flooding in the phases of rice plant vegetation: seedlings, tillering, flowering, and full ripeness of the grain.

In freshly collected soil samples without drying and grinding, we determined di- (FeO) and trivalent (Fe₂O₃) iron in 0.1 N H₂SO₄ at a soil-to-solution ratio of 1: 5 and shaking for five minutes, followed by filtration through a dry ash-free filter with a pore diameter of 3-5 microns. The method is based on forming a soluble complex compound Fe [C₁₀H₈N₂] 32+ being intensely red during the interaction of α, α-dipyridyl (C₁₀H₈N₂ Sigma-Aldrich, USA) with bivalent iron. This compound is stable in the pH range of 3.5-8.5, and the color intensity is proportional to the concentration of iron in the solution. FeO and Fe₂O₃ are determined simultaneously in two portions of 0.1 H₂SO₄ on a spectrophotometer Thermo Scientific GENESYS 10S UV-Vis at a wavelength of 508 nm. In the first portion, FeO was determined, in the second portion – the sum of FeO + Fe₂O₃, with FeO being previously converted into Fe₂O₃ using hydroxylamine hydrochloric acid (H₄CINO). To do this, a buffer acetate solution was added to two portions of the filtrate, and H₄CINO was added to the second portion, after adding α, α-dipyridyl, the volume in a volumetric flask was brought to the line with distilled water, thoroughly mixed, and after 30 min the absorption was measured on a spectrophotometer at a wavelength of 508 nm. In the first determination, the FeO content was determined. The amount of Fe₂O₃ was calculated by means of subtracting it from the results of the second determination and multiplying by a factor

of 1.11 (Novitskii *et al.*, 2009).

The determination of pH and redox potential (Eh, mV) was carried out simultaneously in undisturbed soil composition by a potentiometric method using a Mettler Toledo pH meter (Novitskii *et al.*, 2009). The value of the partial pressure of hydrogen (rH₂) was calculated using Equation 2, introduced by V. M. Clark and B. Cohen:

$$rH_2 = \frac{Eh}{30} + 2pH \text{ at } 20^\circ\text{C} \quad (\text{Eq. 2})$$

This value characterizes the intensity of redox processes in the soil at different pH values of the environment. The predominance of oxidative processes corresponds to rH₂ over 27; of reductive processes – to rH₂ <27; of intensive reductive processes – to rH₂ <20 (Savich, Gukalov, and Polyakov, 2017; Savich, Kaurichev, Shishov, Nikol'skii, and Romanchik, 2004).

The magnetic susceptibility (χ) of the studied soils was measured with a Satis Geo KM-7 kappameter (Czech Republic) (Babanin *et al.*, 1995; Vodyanitskii and Skripnikova, 2000). The measurements were carried out in the field at each site in 15 replicates. The method did not require chemical or physical destruction of soil samples and was applied for the first time under rice cultivation conditions. Single-mode of measurement was used to be reproduced in two stages. The first stage consisted of zeroing the device, which was removed from the studied soil samples and other magnetic or conductive objects at a distance of at least 30 cm. The direct measurement of soil samples characterized the second stage. For this, the gauge sensor was applied to the soil samples taken with a soil drill from under the water layer into a plastic bag, and then the readings were recorded with the KM-7 device. The values of the magnetic susceptibility of soils were expressed in SI units. The sensitivity of the KM 7 device was 1x10⁻⁶ SI units, and the measurement range was ± 999x10⁻³ SI units with automatic switching of the accuracy level, the operating frequency is 10 kHz. The data were exported to a text file by means of the KMdata software and were used for further processing in Microsoft Excel.

3. RESULTS:

The conducted analysis showed that there was a sharp change in oxidative reduction processes (Figure 1). The highest values of the redox potential were noted before their flooding at rH₂ equal to 25-28. After creating the water layer,

the soil potential gradually decreased, reaching its minimum values in the rice flowering phase. During this period, negative values of $E_h = -127 \dots -167$ mV were recorded in the soil layer 0-10 cm in the range of $pH = 6.89-7.36$ units and $rH_2 = 9-10$. The difference in the interval between the redox potential indicators before soil flooding and during the period of maximum development of reductive processes (rice flowering phase) reached 502-630 mV. After the discharge of water from rice fields and drying of the soil, oxidative processes were activated, and the E_h values increased. However, due to the ability of soils to be in a state of complete moisture saturation and increased compaction of the arable layer for a certain time after rice harvesting, the process of oxidation of reduced products is difficult in them.

Different soils have unequal resistance to changes in the redox potential. Before the flooding of paddy fields, the potential difference between the soils of the meadow-boggy and meadow-chnozem types already amounted to 77-88 mV (Table 1).

Table 1. The difference in the oxidation-reduction potential between meadow chernozem and meadow bog soils during the growing season of rice

Rice vegetation phase	Difference E_h , mV	
	Sowing rice 1st year	Permanent sowing of rice
Before the soil is flooded	+88	+77
Seedlings	+152	+138
Tillering	+35	+131
Bloom	-40	-25
Full ripeness of grain	+111	+48

The most pronounced reductive processes were expressed in the meadow-boggy soil at the beginning of the rice-growing season (Plot 2). 30 days after its flooding, which corresponded to the germination phase, the E_h values decreased from 375 to 171 mV, and rH_2 became equal to 17. This indicated strongly reductive conditions in the upper 0-10 cm soil layer. The absence of a sufficiently developed root system in rice plants during this period can cause their suppression or death. The discharge of irrigation water from paddy fields, carried out

during this period according to the agricultural technology of rice cultivation, improves soil aeration, which favorably affects the development of plants.

The best aeration conditions were observed in meadow-chnozem soil. After 30 days of the soil being in a flooded state, E_h in the 0-10 cm layer decreased from 463 to 323 mV at $rH_2 = 24$. This indicated the predominance of a weak, reduced environment in the soil (Plot 1). The same direction of soil processes was observed in the soil under permanent rice cultivation (Plot 5) – from 452 to 309 mV at $rH_2 = 22$, with the only difference was that the E_h values were lower 11-14 mV.

Later, regardless of the type of soil and the duration of rice cultivation, strong anaerobic processes developed in them. Already by the tillering phase of rice plants, rH_2 in soils dropped to 15-16. However, the reductive processes reached the greatest intensity after 90 days of soil flooding, i.e., in the flowering phase. Moreover, in the meadow-boggy soil, the E_h values were lower than in the meadow-chnozem soil. The potential difference between them equaled 25-40 mV.

After the cessation of water supply to the paddy fields and the creation of aerobic conditions in the phase of complete ripeness of the grain, the redox potential increased more intensively in the meadow-chnozem soil, which indicated rather rapid oxidation of the reduced compounds. Simultaneously, the oxidation processes in the soil under permanent rice were weaker than in rice crop rotation conditions. Lower values indicated this for E_h (236 versus 326 mV) and rH_2 (24 versus 19).

In non-flooded paddy fields under perennial grass crops, the oxidative regime was maintained throughout the irrigation period. Simultaneously, in the meadow-boggy soil, aerobic processes developed slower (Plot 4), as indicated by the low values of the redox potential, ranging from 388 to 440 mV at $pH = 7.10-7.47$ units and $rH_2 = 27-29$ (Figure 1).

The best conditions for aeration under perennial grasses were found in the meadow-chnozem soil (Plot 3). The E_h values during the entire measurement period varied in the 0-10 cm layer from 410 to 470 mV at $pH = 6.59-7.57$ units and $rH_2 = 28-30$. Compared to Plot 4, the E_h value was 20-55 mV lower.

Thus, the most intensively reductive conditions develop in the meadow-boggy soil of

rice fields than in the meadow-chnozem soil. The maximum intensity of reductive processes in flooded soils of rice agroecosystems is achieved by the flowering phase of the rice plants (Eh equals from -127 to -167 mV, pH = 6.89-7.36 units, rH_2 9-10).

Studies showed that the development of reduction processes led to the transformation of poorly soluble Fe_2O_3 compounds into more active FeO reaction forms (Figures 2, 3). After a decrease in the redox potential, the content of reduced iron in the studied soils and the quantitative ratio of FeO: Fe_2O_3 increased sharply, which indicated the creation of an anaerobic environment. The intensity of the accumulation of bivalent iron in the soil increased with the growth of reduction processes in it. During the period of anaerobiosis, the content of Fe_2O_3 in the soil decreased, and when anaerobic conditions changed with aerobic ones, their amount increased again.

Different modes of oxidation-reduction conditions in meadow-chnozem and meadow-boggy soils had a different effect on the dynamics of the content of iron compounds in them. A weak manifestation of reductive processes characterizes the meadow-boggy soil even before its flooding (rH_2 = 25). The total content of ferrous and ferric iron in the arable (0-20 cm) and sub-arable (21-40 cm) soil layers during this period was 207.24 and 191.41 mg/100 g, respectively (Plot 2). Active iron was represented by compounds of the trivalent form (FeO: Fe_2O_3 < 1.0). Simultaneously, in spring, before the soil was flooded, reasonably high content of under-oxidized iron was found not only in the arable layer but also in the subsoil. The share of FeO content was 8-14%, and Fe_2O_3 amounted to 86-92% of the total FeO + Fe_2O_3 . Compared with meadow-chnozem soil, the FeO content was 3.0-4.5 times higher in rice crop rotation fields (Plot 1) and 1.5-2.0 times higher under permanent rice cultivation (Figures 2 and 3).

A month after the meadow-boggy soil flooding, there was a sharp increase in FeO content and a decrease in the amount of Fe_2O_3 , especially in the upper 0-10 cm layer (FeO: Fe_2O_3 = 1.16). According to rice cultivation technology, this is despite the periodic discharges of water from the paddy fields in the phase of plant emergence, aimed at airing and enriching the soil with air oxygen. Although in the deeper layers of the soil, weak oxidizing conditions persisted: the ratio of FeO: Fe_2O_3 in 11-20, 21-30, and 31-40 cm soil layers equaled 0.83, 0.62, and 0.42, respectively.

In the tillering phase, the accumulation of reduced iron in the soil continued, reaching its maximum for rice flowering - FeO = 269.38 mg/100 g at Eh = -127 mV and pH = 7.36 units, rH_2 = 10. Simultaneously, as the reduction processes increased, the amount of Fe_2O_3 in the soil sharply decreased, especially in the upper layers of 0-10 and 11-20 cm. During the period of the highest intensity of the reduction regime, which corresponded to the phase of plant flowering, the Fe_2O_3 content in the 0-10 cm layer was 18.96 mg/100g, and the FeO: Fe_2O_3 ratio increased to 14.0. The anaerobic environment persisted in the lower soil layers at 11-20, 21-30, and 31-40 cm. However, the reductive processes in those layers were less pronounced (FeO: Fe_2O_3 = 3.2, 1.8, and 1.0, respectively).

Based on the statistical evaluation of the experimental data, a high negative correlation was established between Eh and the content of FeO in meadow-boggy soil, equal to $r = -0.83$, as well as a positive correlation with Fe_2O_3 $r = 0.79$, and a strong correlation between FeO and Fe_2O_3 ($r = -0.97$).

A completely different oxidation-reduction regime in the rice field developed in meadow-chnozem soil (Plots 1, 5). Before sowing and flooding the paddy field, the total active iron content in the arable and subsoil layers was 222.07 and 199.06 mg/100 g, respectively (Plot 1). Simultaneously, the share of FeO content accounted for 2.01-3.73% and Fe_2O_3 – 96-98% of the total FeO + Fe_2O_3 . The proportion of FeO content was 1.5-2.0 times higher (4.02-5.40% of the total FeO + Fe_2O_3) than under rice crop rotation conditions in the soil under permanent rice cultivation. Regardless of the duration of rice cultivation, most of the undeoxidized iron was contained in the 0-10 cm layer and decreased by two times with the soil depth (Figures 2, 3).

If, before the meadow-chnozem soil flooding, the FeO content was low compared to the meadow-boggy soil, then after creating a layer of water in the paddy fields, its amount increased. However, ferric oxides still predominated in the seedling phase. This can be explained by the fact that there were discharges of water from paddy fields during this period, and the soil was well enriched with air oxygen. Nevertheless, after creating a permanent layer of water, from the tillering phase to the flowering of rice plants, an accumulation of bivalent active iron and a decrease in trivalent active iron content were noted. The maximum content of reduced iron was reached by the rice flowering phase 152.64-165.84 mg/100 g at Eh = -152 ...2

167 mV, pH = 6.89-7.10 units, and $rH_2 = 9$. The amount of Fe_2O_3 during this period decreased to 55.00-58.29 mg/100 g, and the ratio of FeO:Fe₂O₃ in layers 0-10 and 11-20 cm was 2.77-2.80 and 1.66-2.40, respectively. This indicated that recovery processes were taking place in the soil. However, at the lower soil layers, their tension noticeably weakened. The narrow range of FeO evidenced this: Fe₂O₃ ratios in the layers 21-30 and 31-40 cm, equal to 0.17-0.23 and 0.07-0.17, respectively, indicating the predominance of oxidizing conditions in the soil.

After the water was discharged from the paddy fields, the reduced iron was gradually oxidized by atmospheric oxygen. At the same time, in the meadow-boggy soil, the oxidation process in the 0-10 cm layer was slower than in the meadow-chnozem soil: FeO: Fe₂O₃ = 7.4 at Eh = 215 mV versus FeO: Fe₂O₃ = 1.3-2.3 at Eh = 236-326 mV.

Regardless of the duration of rice cultivation, the direction of the dynamics of active forms of iron compounds in the growing season of rice was the same. In the meadow-chnozem soil of the rice crop rotation, negative correlations were established between the indicators Eh and FeO ($r = -0.89$), FeO and Fe₂O₃ ($r = -0.74$), positive between Eh and Fe₂O₃ ($r = +0.70$). In the soil of permanent rice cultivation, correlations between these indicators equaled -0.89, -0.79, and +0.73, respectively.

In non-flooded soils under perennial grass crops, the ferric iron content dominated throughout the observation period, and the oxidative regime prevailed in them (Figures 1-3). In the meadow-boggy soil (Plot 4), oxidative processes were less developed than in the meadow-chnozem soil (Plot 3). This was indicated by a lower Eh in the 0-10 cm layer, fluctuating in the range 388-440 mV at pH = 7.10-7.47 units and $rH_2 = 27-29$, and increased content of FeO in the soil in the range from 10.10 to 41.92 mg/100 g.

The best oxidizing conditions under crops of perennial grasses developed in meadow-chnozem soil. During the entire measurement period, the Eh values in the 0-10 cm layer varied in a small range of 410-470 mV at pH = 6.59-7.57 units and $rH_2 = 28-30$. Compared to the meadow-boggy soil, the FeO content was lower by 33%, in layers at 11-20 and 21-30 cm, it was lower by 41%, and in layers at 31-40 cm by 51%. Simultaneously, the content of Fe₂O₃ was higher in the 0-10 cm layer by 9.72%, in the 11-20 cm layers by 8.63%, 21-30 cm by 6.35%, and in the

31-40 cm layers by 12.67%.

In non-flooded meadow-chnozem and meadow-boggy soils under perennial grasses, a negative correlation between Eh and FeO ($r = -0.84$ to -0.89) was noted.

Studies showed that the dynamics of Eh and active forms of iron compounds during the flooding of soils in rice fields are associated with a change in the value of the magnetic susceptibility χ , which decreased under anaerobic conditions. Its minimum values were recorded during the period of maximum reduced iron content at low Eh values, i.e., in the flowering phase of rice plants. During this period, χ indices in the flooded soil varied in the range from 0.059-0.081 in the 0-10 cm layer to $4.7-6.6 \times 10^{-5}$ S.I. units in the lower layers, i.e., 60 days after the emergence of rice seedlings, they decreased by 1.5-2.0 times (Figure 4).

The nature of magnetic susceptibility dynamics in meadow-chnozem soil under permanent rice cultivation conditions and crop rotation was approximately the same. However, during the period of maximum intensity of reductive processes, lower values of χ were achieved with permanent rice cultivation (Figure 4). This is explained by the low content of organic matter in the soil, which catalyzes biochemical reduction reactions during the period of its flooding (Sheudzhen *et al.*, 2019).

The highest χ values are confined to the upper 0-10 cm soil layer; in the 11-20 cm layer, they are 1.5-2.0 times lower. Their decrease was also noted in the lower layers (at 21-30 and 31-40 cm). The χ value is always higher in the surface horizons, where the content of humic acids is increased since the latter can be catalysts for the ferromagnetisation of weakly magnetic iron compounds (Babanin *et al.*, 1995).

When oxidizing conditions are created in the soil, the magnetic susceptibility increases. After the discharge of water from paddy fields relative to the rice flowering phase, the χ value increased in the 0-10 cm layer by 17-25%, in the 11-20 cm layer by 42-47, in the 21-30 cm layer by 12-26, and in the 31-40 cm layer by 10-18%.

The largest values of χ were formed in the meadow-chnozem soil. On average, during the growing season of rice, this indicator was higher than in the meadow-boggy soil by 16.0-54.0%. The lower χ values of the meadow-boggy soil reflect the low content of crystallized highly magnetic minerals (Babanin *et al.*, 1995). This is due to the dissolution of iron-containing minerals

under reductive conditions (Grimley and Vepraskas, 2000; Van Bodegom, Van Reeve, and Van Der Gon, 2003).

The aerobic conditions created by the accompanying rice crop rotation favor the formation of more magnetic iron-bearing minerals (Figure 4).

In meadow-chnozem soil, the indicators of the magnetic susceptibility of soil under perennial grasses are more stable throughout the observation period and higher in the 0-10 cm layer by 3.2×10^{-5} , in the 11-20 cm layer by 5.5, in the 21-30 cm layer by 3.4, and in the 31-40 cm layer by 4.2×10^{-5} S.I. units than in flooded rice field soil. Accordingly, they are higher in the meadow-boggy area by 1.8×10^{-5} , 1.7, 1.4, and 1.1×10^{-5} S.I. units. Simultaneously, a general pattern is observed: the smallest indicators of magnetic susceptibility, both under oxidative and reducing modes, were recorded in meadow-boggy soil.

Hence, it follows that in the aerobic period of the rice field, conditions appear that determine the possibility of the formation of more magnetic iron-containing compounds in soils. When the moistening period is changed to desiccation, newly formed ferromagnets are found in them (Zonn, 1982; Vodyanitskii, Morgun, Rummyantseva, Obydenova, and Chapygina, 2009).

4. DISCUSSION:

The practice of rice cultivation, literature data, and our research indicates that the technology of rice cultivation, which provides for the maintenance of the rice field for the main part of the growing season of rice under a layer of water, is associated with a change in the oxidation-reduction conditions in the soil (Bahmanyar, 2007; Sheudzhen and Gutorova, 2020; Sheudzhen *et al.*, 2019; Annisa and Nursyamsi, 2016; Goton and Patrick, 1973). The flooding factor largely determines the exclusive orientation of soil-forming processes. One of the decisive conditions for high soil fertility in rice fields is to ensure a favorable redox potential, which is regulated by measures that traditionally include a balanced use of mineral fertilizers, replenishment with fresh organic matter, scientifically substantiated introduction of crop rotation with the inclusion of perennial grasses, soil cultivation techniques for them. Oxidation during the inter-irrigation period and the accumulation of chemically bound oxygen in

them, lowering the groundwater level. In this regard, diagnostic indicators are needed to characterize the oxidation-reduction regime of soils in rice agrocenoses. The previous section considered the dynamics of the redox potential and compounds of active forms of iron, which fully reflect the oxidation or reduction state of the rice field. The literature highlights the relationship between the redox potential and ferrous iron content in soils under rice. The data we obtained do not disagree with the literature (Annisa and Nursyamsi, 2016; Akter *et al.*, 2018; Gardiner and James, 2012). W. Annisa and D. Nursyamsi (2016) showed a negative correlation between the Eh value and the Fe^{2+} concentration equal to $r = -0.856$.

We analyzed the possibility of using the value of the magnetic susceptibility χ as an indicator of the redox state of soils in rice fields. The literature mainly describes the profile distributions of magnetic susceptibility. It has been shown that in rice soils, there exists a more pronounced profile differentiation of iron oxides and a low magnetic susceptibility in comparison with well-drained soils (Zhang and Gong, 1993; Lu, Zhu, and Yu, 2012; Han and Zhang, 2013; Huang *et al.*, 2018).

From the studies carried out, it follows that the magnitude of the magnetic susceptibility can be judged on the direction of the redox processes occurring in the flooded soils of rice fields. Its minimum values coincide with the maximum FeO content in them at negative Eh values in the flowering phase of rice plants:

$\chi = 5.9 \times 10^{-5}$ SI units, FeO = 269.38 mg/100 g, $\text{Fe}_2\text{O}_3 = 18.96$ mg/100 g, Eh = -127 mV, pH = 7.36 units, $r\text{H}_2 = 10$ for meadow-boggy soil;

$\chi = 7.6-8.1 \times 10^{-5}$ SI units, FeO = 152.64-165.84 mg/100 g, $\text{Fe}_2\text{O}_3 = 55.00-58.29$ mg/100 g, Eh = -152...-167 mV, pH = 6.89-7.10 units, $r\text{H}_2 = 9$ for meadow-chnozem soil.

Based on the statistical evaluation of the experimental data, the dependence of the χ values on the indicators of the redox regime of soils was noted (Table 2).

Table 2. Correlation between the value of magnetic susceptibility and indicators of the oxidation-reduction regime of soils ($p < 0.05$, $n = 35$)

Plot/Indicator	FeO	Fe_2O_3	Eh
Plot 1. Meadow-	-0.69	0.76	0.72

chernozem soil. Sowing rice 1st year after winter wheat			
Plot 2. Meadow- boggy soil. Sowing rice in the 1st year after a busy fallow (winter wheat)	-0.84	0.77	0.66
Plot 3. Meadow- chernozem soil. Sowing perennial grasses of the 2nd year	0.41	0.90	-0.28
Plot 4. Meadow- boggy soil. Sowing perennial grasses of the 2nd year	0.27	0.83	-0.40
Plot 5. Meadow- chernozem soil. Permanent rice cultivation for 80 years without fertilization (since 1937)	-0.80	0.74	0.75

During the flooding of the meadow-boggy soil, correlations with FeO ($r = -0.84$) were revealed, weaker with Fe₂O₃ ($r = +0.77$) and Eh ($r = +0.66$), while during the flooding of the meadow-chernozem soil we discovered positive relations with Fe₂O₃ and Eh ($r = +0.76$ and $+0.72$, respectively) and negative relations with FeO ($r = -0.69$). Under conditions of permanent rice cultivation, we discovered relations with FeO, Fe₂O₃, and Eh: -0.80 , $+0.74$, and $+0.75$ respectively.

The χ values increase and are more stable in dynamics with the predominance of aerobic processes in soils. In meadow-boggy and meadow-chernozem soils under perennial grasses, the highest correlation coefficients were noted between the χ value and the Fe₂O₃ content, equal to $+0.83$ and $+0.90$, respectively.

Thus, with the flooding of soils in rice fields, the value of the magnetic susceptibility decreases, which indicates a decrease in the redox potential and an increase in the content of reduced iron.

5. CONCLUSION:

The results demonstrates the possibility of using one of the characteristics of the magnetic properties of soils, the magnitude of the magnetic susceptibility, to diagnose the oxidation-reduction

state of rice agrocenoses. This is the first time such research has been conducted in rice fields.

The reductive processes that occur in the soils of rice fields after flooding lead to the transformation of poorly soluble Fe₂O₃ compounds into more active reaction forms of FeO. The maximum content of FeO and the minimum amount of Fe₂O₃ were recorded during the period of negative values of the redox potential – the phase of flowering of rice plants. During this period, in the flooded meadow-boggy soil, the content of reduced iron reaches 269.38 mg/100 g, the ratio FeO:Fe₂O₃ = 14.0, Eh = -127 mV, pH = 7.36 units, rH₂ = 10; meadow chernozem – 152.64-165.84 mg/100 g, FeO:Fe₂O₃ = 2.77-2.80, Eh = $-152 \dots -167$ mV, pH = 6.89 ... 7.10 units, rH₂ = 9. At the same time, in the meadow-chernozem soil of permanent rice sowing, the dynamics of Eh and iron compounds are similar to the fields of rice crop rotation. In the soil of permanent rice cultivation, the dynamics of Eh and iron compounds are similar to the fields of rice crop rotation. In non-flooded soils of rice fields under perennial grasses, the oxidative regime prevails, and the transformation of iron compounds does not occur.

The minimum values of the magnetic susceptibility (χ) coincide with the maximum content of ferrous iron in the flooded soil and a low redox potential, which corresponds to the flowering phase of rice plants. The correlation (determination) coefficients between the value of χ and Eh, FeO and Fe₂O₃ are $r = +0.66 \dots +0.75$ ($r^2 = 0.44 \dots 0.56$); $r = -0.69 \dots -0.84$ ($r^2 = 0.48 \dots 0.71$) and $r = +0.74 \dots +0.77$ ($r^2 = 0.55 \dots 0.59$), respectively. Indicators of magnetic susceptibility increase in the soil under crops of perennial grasses with a predominance of oxidative processes. The correlation coefficient between χ and Fe₂O₃ is $r = +0.83 \dots +0.90$ ($r^2 = 0.69 \dots 0.81$).

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Legend: plot 1 meadow-chnozem soil (rice sowing in the 1st year after a busy fallow); plot 2 meadow-boggy soil (rice sowing in the 1st year after a busy fallow); plot 3 meadow-chnozem soil (sowing of perennial grasses of the 2nd year); plot 4 meadow-boggy soil (sowing of perennial grasses of the 2nd year); plot 5 meadow chernozem soil (rice monoculture since 1937).

Figure 1. Dynamics of the redox potential in the soils of rice fields

Figure 2. Dynamics of the ferrous iron content in the soils of rice fields

Figure 3. Dynamics of the content of ferric iron in the soils of rice fields

Figure 4. Change in magnetic susceptibility in the rice field soils