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ZENOVIIY PANKIV\*, TARAS YAMELYNETS\*

## FERRUM CONCRETIONS FORMS IN THE MOLLIC GLEY SOILS OF LOW (MALE) POLISSYA

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*Abstract.* In the humid conditions, the most common ground forms are the ferruginous ones: ferum concretions, marsh ore, ocher spots, etc. Mollic gley soils are widely spread along the periphery of marshes and are formed under the influence of mollic and gley processes on various soil-forming rocks under conditions of sporadically pulsating water regime and excessive moisture under the meadow and swamp biocenoses. The ferrum concretions are characteristic of all genetic horizons of mollic gley soils, except for the soil-forming rock, and their content ranges from 3.3% in the mollic to 47.1% in the lower transitional horizon. The gross iron content in the fine mollic gley soils, as well as in the ferrum concretions forms, increases with depth, and the maximum values are characteristic of the lower transition horizon. The lowest values of the gross iron content are characteristic of the fine soil-forming rock (16.0 mg / 100 g soil) and the mollic soil (66.4 mg / 100 g soil). It was established that the gross chemical content of the ferrum concretions forms is dominated by the iron oxides with the highest content in the ferrum concretions of the mollic soils (48.75%). Also the ferrum concretions forms of iron are characterized by a rather high content of aluminum oxides (5.59–7.92%). The highest values of the accumulation coefficient are characteristic of the iron oxide ( $K_x = 7.21-2.58$ ), which confirms the hypothesis of the dominant role of its compounds in the formation of the ferrum concretions forms.

**Keywords:** ferrum concretions forms, mollic gley soils, Low (Male) Polissya, the accumulation coefficient

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\* Ivan Franko National University of Lviv, Faculty of Geography, 41 Doroshenko Street, 79000 Lviv, Ukraine. Corresponding author's e-mail: [taras.yamelynets@gmail.com](mailto:taras.yamelynets@gmail.com)

## INTRODUCTION

The study of soils genesis and their properties requires a detailed study of concretions forms, and in humic conditions, the most common soil concretions forms are the ferruginous ones. Iron is characterized by variable valency, the ability to form complex compounds and form the concretions forms – formed clusters in the soil mass of different shapes and chemical composition substances, which are the result of the soil formation process (Gryn 1974, Rozanov 1983, Cornell and Schwertmann 2003, Jaworska *et al.* 2016, Orzechowski *et al.* 2018). Typical forms of the ferruginous are: ferrum concretions, marsh ore, ortstains, ortzands, clusters, pseudo fibers, and ochre spots. The value of iron in acidic unsaturated humus soils can be compared with the role of calcium in black soils, because it performs a number of important functions and serves as a basis for the diagnosis of soil-forming processes: amorphous and weakly crystallized iron performs the function of a structure-forming agent in the soil; iron in its exchange mode is absorbed by plants, protecting them from chlorosis; iron-organic complexes reduce the irreversible binding of phosphorus and promote its availability for plant nutrition; iron compounds as the structural agents improve the physical properties of acidic soils (Duchaufour 1970). Under certain conditions, especially at deposition and the formation of concreting ortstain, ortzand and pseudo fiber layers, iron affects the filtration and causes the emergence of permanent or seasonal overflow, and the restorative forms can be toxic to plants. Accumulation or eluvium of free iron is associated with the manifestation of a number of elemental soil processes that determine the formation of genetically independent soil types (Duchaufour and Sochiers 1978, Zonn 1982, Jaworska *et al.* 2016).

Establishment of soil areas with formed iron forms (mollic ore, ferrum concretions) was carried out by human before the formation of knowledge about soils and their use as the main means of production in agriculture, since such forms served as the raw materials for ancient metallurgy and blacksmithing. The local population has found out that the clusters of iron forms are confined to the grounds of the overflowed territories, and the places of their past mining are reflected in the names of the settlements (Ruda, Rudno, Rudka, etc.) or localities. With the development of genetic soil science, the study of iron in soils occurred in two directions – morphological and geochemical (Duchaufour and Sochiers 1978, Zonn 1982).

In the history of the iron studying methods in soils, there are three stages: 1 – determination of the gross content and profile distribution of iron with division into oxidizing and acidic compounds; 2 – mineralogical and chemical study of iron-containing minerals and solubility of mobile iron in the organic mineral compounds, mineral acids of different concentrations; 3 – differentiated mineralogical, chemical and spectrometric study of iron compounds for the purpose of distinguishing its forms by the degree of crystallization and identifica-

tion by their X-ray diffraction and micro-morphological methods (Zonn 1982, Zeidelman 2001, Kubienna 1938, Tamm 1922, Kanivets 1975, Orzechowski *et al.* 2018). Moreover, soils formed from glacial deposits often show genetic heterogeneity and lithological discontinuity (Birkeland 1999, Kühn 2001). Defining the relationship between lithogenesis and pedogenesis is one of the key problems on studying those soils. Evaluating the soil-formation pattern and the origin of soils based on the chemical composition of the soil mass requires reference to soil parent materials (Arduino *et al.* 1986, Jaworska *et al.* 2016).

During the study of soils in Ukraine, little attention was paid to the study of iron formation. Most information about areas of distribution and concretions forms is presented in the morphological descriptions of the profiles without conducting special laboratory studies. There were no special studies of the ferrum concretions forms in the Ukrainian soils, which is a significant disadvantage of the established genesis of hydromorphic and semi-hydromorphic soils.

The purpose of the study is to establish the characteristics of the profile distribution of iron ore forms formation in the mollic gley soils, to study the fractional composition of ore within the limits of genetic horizons and their chemical properties. The object of the study is the iron ore forms formation in the mollic gley soils of Male Polissya, the subject of the study – the features of ferrum concretions profile distribution, their fractional composition within the genetic horizons, the gross chemical composition of ore and fine soil.

## MATERIALS AND METHODS

The obtained results are based on our own field morphological and laboratory-analytical studies. In the field conditions, the morphological characteristics of the mollic gley soil profile were studied and the regularities of ore deposits distribution, their fractional composition within the limits of the genetic horizons were established. The ferrum concretions were backwashed through the sieves with specified diameters (0.25–10.00 mm) to obtain the fractional composition of the ferrum concretions forms in the mollic gley soils (Kachynskyi 1965). In the selected samples of soils and ore forms there was determined the total iron content and their gross chemical composition by Kirsanov's method (Arinushkina 1970). According to the gross chemical composition of the fine and ferrum concretions in different genetic horizons, the accumulation coefficient ( $K_x$ ) and the ratio of Fe : Mn was calculated (Zaidelman 2001). In order to establish the relative accumulation of chemical elements and its impact on the formation of soil concretions, the accumulation coefficient ( $K_x$ ) is calculated. This coefficient is calculated as the ratio of the gross content of specified chemical element in the soil formation to its content in the fine fraction. If the value of  $K_x$  is greater than 1, it confirms its accumulation in the soil concretions (Zaidelman 2001).

## RESULTS

Based on the field studies, it has been found that the ocher spots and ores are characterised to the entire profile of turfy gley soils. However, the most available for research are the iron ore forms. The ferrum concretions, along with the mollic ore and ferruginous crust, refer to the oval flat, large, iron-bearing concretions. The ferrum concretions are different from the mollic ore by larger size (from 5 to 30 cm), they are found throughout the whole profile, while the mollic ore – only in the surface horizon and it is formed in the conditions of close occurrence of groundwater with high content of Fe (20–50 mg/l) (Zaidelman 2001).

The starting basis for the formation of iron forms is the iron oxide, which occurs in various forms and minerals. As a result of the combined action of various processes (oxidation, hydrolysis, dehydration, destruction, etc.), compounds are formed, which leads to the formation of minerals (goethite, hematite, etc.), which are the basis for formation of iron forms (Vodyanitsky 1992, 2002, Cornell and Schwertmann 2003).

The mollic gley soils, which are characterized by the ferrum concretions forms, are distributed along the periphery of swamps, lots of which are found in the western region of Ukraine (Polissya lowlands, Male Polissya, and Precarpathians). They were formed at the expense of mollic and gley processes and mineralization on various soil-forming rocks under conditions of the excess soil surface humidification and sporadic-pulsating water regime under the meadow, meadow and swamp biocenoses.

In order to study the mollic gley soils, we have laid a key site in the suburbs of Birky village, Yavoriv district of Lviv region, where the laying of soil sections and their morphological research were conducted. Below there is a description of the soil profile, laid 500 m south of the western outskirts of the Birky village (Fig. 1).

**O (0–7 cm)** is a turf, of the light gray color with a large number of the ocher spots of oval and oblong form, occasionally there are black spots and rust (0.1–1.5 cm). Tightly intertwined with small roots. Gleying at the surface is intense. The transition to the next horizon is wavy and clear.

**Ag (7–27 cm)** is a humus-accumulative gleyed horizon of various colors; on a gray background there is a considerable quantity of ore ocher spots in diameter from 0.2 to 1 cm, and of black cemented oval ore accumulation (0.5–1 cm). Compacted, fresh, the greyish quartz grains are observed on a gray background of structural divisions. The structure is lumpy, permeated with small roots, the transition is wavy and clear.

**ABg (27–54 cm)** – the rock is humus gleyish (ore-bearing horizon). The color is brownish ocher with black, dark gray shades. A considerable amount of iron-bearing ores in diameter from 1 cm to 2–3 cm. The structure is small prismatic, dense. The small roots of plants, in the lower part of the wormhole, are painted with ferruginous-humus flows. The transition is sharp and straight.



Fig. 1. Profile of the mollic gley medium-sandy soils on the water-glacial sediments bedded with the glauconite sands

**Cg (54–88 cm)** is a gleyish rock, fluvioglacial gleyed sands of dirty-greyish color with brown-ocher spots of an oval and oblong form, permeated with corneal marsh plants, which are stained with iron flows of an ocher color.

**RG (> 88 cm)** – underlying rock, glauconite sands of greenish, pale blue color with the inclusion of greyish marl, permeated with roots which, under the condition of a reduced level of groundwater, have brown-ocher coloration.

A characteristic feature of the studied soils is the presence of the ferrum concretions forms within the entire profile, with the exception of the soil-forming rock. The content and size of the ferruginous forms increases with depth. Ferruginous forms in the mollic gley soil are established in three horizons: O – 3.3%, Ag – 12.6%, ABg – 47.1% (Table 1).

Table 1. Percentage and fractional composition of the ferrum concretions forms in the mollic gley soils

The name of the genetic horizon and its parameters	Fraction size (cm)	Fraction content (%)
O (0–7 cm)	0.1–0.7	47.5
	0.8–1.4	21.5
	1.5–2.1	6.8
	2.2–2.8	24.2
Ag (7–27 cm)	0.1–0.7	6.6
	0.8–1.4	13.0
	1.5–2.1	30.5
	2.2–2.8	49.9
ABg (27–54 cm)	0.1–1.4	35.0
	1.5–3.6	31.3
	3.7–5.4	8.5
	5.5–7.2	25.2

It has been established that the size of the ore forms fractions increases with depth (Table 1). If in the horizon O the maximum size of forms was 2.5 cm (Fig. 2), then in the horizon ABg – 7.2 cm (Fig. 3). Within the O horizon, small ore forms predominate in size from 0.1 cm to 0.7 cm – 47.5% of their total, as well as the size from 2.2 to 2.8 cm (24.2%) (Table 1). Instead, in the Ag horizon, the largest proportion of the ore forms is from 2.2 to 2.8 cm (49.9%), and a fraction of 0.1 to 0.7 cm is only 6.6%. In the ABg horizon, the size of the new iron forms is the largest (Fig. 3). It was determined that more than 65% occupy ferrum concretions in the size from 0.1 to 3.6 cm, and 25.2% – with the size of more than 5.5 cm (Table 1). Also, in the ABg horizon, the ferrum concretions forms content is the largest (47.1%), and within its limits there are large ferrum concretions in the size of more than 3.6 cm (33.7%) (Fig. 4).



Fig. 2. The fractional composition of the ferrum concretions forms in the O horizon of the mollic gley soils





Fig. 3. The fractional composition of the ferrum concretions forms in the Ag horizon of the mollic gley soil



Fig. 4. The fractional composition of the ferrum concretions forms in the ABg horizon of the mollic gley soil

In order to study the properties of the ferrum concretions forms, we conducted a chemical and physical-chemical analysis. Kirsanov's method determined the content of gross iron in the fine mollic gley soils and ferrum concretions forms (Tables 2, 3).

Table 2. Gross iron content of the ferrum concretions forms of the mollic gley soils

The name of the genetic horizon and its parameters	Gross iron content, mg/100 g of soil
O (0–7 cm)	170.4
Ag (7–27 cm)	179.2
ABg (27–54 cm)	233.6

Table 3. Gross iron content of the fine mollic gley soils

The name of the genetic horizon and its parameters	Gross iron content, mg / 100 g of soil
O (0–7 cm)	66.4
Ag (7–27 cm)	112.0
ABg (27–54 cm)	147.2
Cg (54–88 cm)	16.0

The obtained results indicate that the gross iron content, both in the fine mollic gley soils, and in the ferrum concretions forms, increases with depth, and the maximum values are characteristic of the ABg horizon. The smallest values of the gross iron content are characteristic of the fine soil-forming rock (16.0 mg / 100 g soil) and the mollic soils (66.4 mg / 100 g of soil). In the ferrum concretions forms, the gross iron content is relatively large, and the maximum values of total iron content (233.6 mg / 100 g soil) are characteristic of the ferrum concretions of the ABg horizon, which allows us to assume the increase in iron content with an increase in the size of the ferrum concretions forms fractions.

The results of gross chemical analysis, which serve as the basis for calculating various ratios and coefficients that are the diagnostic features of soil-forming processes, are extremely important for the study of the mechanisms of ferrum concretions forms formation. The results of the gross chemical composition of the fine soil and the ferrum concretions forms are given in Tables 4, 5.

Table 4. The gross chemical composition of the ferrum concretions forms of the mollic gley soils, % in recalculation on the calcined weight

The name of the genetic horizon	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	MnO	K <sub>2</sub> O	Na <sub>2</sub> O
O (0–7 cm)	39.84	7.92	48.75	0.13	3.75	0.67	0.0	0.28	0.20
Ag (7–27 cm)	47.09	7.48	43.04	0.13	2.41	0.66	0.09	0.34	0.28
ABg (27–54 cm)	49.40	5.59	41.70	0.02	1.35	1.40	0.05	0.30	0.18

Table 5. The gross chemical composition of the fine mollic gley soils, % in recalculation on the calcined weight

The name of the genetic horizon	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	MnO	K <sub>2</sub> O	Na <sub>2</sub> O
O (0–7 cm)	83.78	4.39	6.76	0.29	1.20	0.87	0.54	0.39	0.27
Ag (7–27 cm)	83.61	5.33	9.25	0.36	1.24	1.14	0.0	0.45	0.32
ABg (27–54 cm)	73.62	5.18	16.15	0.12	1.78	3.03	0.0	0.32	0.24
Cg (54–88 cm)	96.32	0.92	1.31	0.07	0.35	1.07	0.03	0.28	0.21

The results of the gross iron chemical composition of the ferrum concretions forms indicate that Fe<sub>2</sub>O<sub>3</sub> is dominant in their composition, with the highest



content (48.74%) in the turf. With the depth of iron oxides in the ferrum concretions slightly decreases and in the ABg horizon is 41.7%. In contrast, the ferrum concretions within the mollic soils have the smallest content of  $\text{SiO}_2$  (39.84%), and with depth the content of silica in the ferrum concretions is increased and its largest value (49.4%) is characteristic of the iron forms in the ABg horizon. Also, the ferrum concretions forms are characterized by a high content of aluminum oxide, the content of which decreases from 7.92% in the ferrum concretions of the mollic soils to 5.59% in the ABg horizon.

The gross chemical composition of the fine mollic gley soils is exclusively dominated by silica with the highest content (96.32%) in the soil-forming rock (water-glacial deposits). In the fine mollic soils the content of silica is 83.78%, and in the fine soil of the ABg horizon is the smallest (73.62%). The gross content of the iron oxides in the investigated fine soil gradually increases with the depth from 6.76% in the mollic soils to 16.15% in the ABg horizon. The smallest content of  $\text{Fe}_2\text{O}_3$  is characteristic of the fine soil-forming rock (1.31%). Similar patterns of the profile distribution have the gross  $\text{Al}_2\text{O}_3$  content in the fine mollic gley soil.

In order to establish the relative accumulation of various chemical elements and to identify their role in the soil forms formation, it is suggested to use the accumulation coefficient ( $Kx$ ), which is calculated according to the formula:  $Kx = C_{\text{Conc.}} : C_{\text{Frac.}}$ , where  $C_{\text{Conc.}}$  and  $C_{\text{Frac.}}$  are the element content ( $x$ ) in the concretions and in the fine soil (Zaidelman 2001).

The basis for calculating the accumulation coefficient ( $Kx$ ) is the results of the gross chemical composition of the ferrum concretions and fine soil in different genetic horizons (Table 6).

Table 6. The accumulation coefficient ( $Kx$ ) of elements in the mollic gley soils

The name of the genetic horizon	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{TiO}_2$	CaO	MgO	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$
O (0–7 cm)	0.48	1.80	7.21	0.45	3.13	0.77	0.72	0.74
Ag (7–27 cm)	0.56	1.77	4.33	0.36	1.94	0.58	0.76	0.88
ABg (27–54 cm)	0.67	1.08	2.58	0.17	0.76	0.46	0.94	0.75

Calculations show that the greatest value of the accumulation coefficient ( $Kx$ ) is characteristic of the iron oxide, and its maximum value ( $Kx = 7.21$ ) is characteristic of the mollic horizon, in the direction towards the rock the value of the coefficient is gradually reduced to  $Kx = 2.58$  in the ABg horizon. Smaller values of the accumulation coefficient ( $Kx = 1.08$ – $1.80$ ) are characteristic of the aluminum oxide, which confirms the hypothesis of the dominant role of iron compounds in the formation of the ferrum concretions forms. For the upper humus horizons (O and Ag), the relative accumulation of calcium ( $Kx = 1.94$ –

3.13) is characteristic due to the biological circulation of this element under the meadow biocenoses.

When studying concretions of different genesis it is important to characterize the ratio of Fe : Mn objectively. To characterize this ratio, the percent abundance of these elements (PAE) in the soil was used as the reference value, that is,  $Fe_{PAE} : Mn_{PAE} = 3.8 : 0.085 = 45$ . On the basis of this value, the ratio of Fe : Mn  $< 45$  is assumed to be low and the values of Fe : Mn  $> 45$  – high (Zaidelman 2001).

The ratio value of Fe : Mn in the ferrum concretions forms ranges from 479 in the O horizon to 834 within the ABg. These ratios are very high, since they are about 20 in the ortstains and are characterized as low. Consequently, the high ratio values of Fe : Mn confirm that the iron oxides play the dominant role in the ferrum concretion forms formation.

## CONCLUSIONS

Ferrum concretion forms are characteristic of the mollic gley soils, which are distributed along the periphery of marshes and are formed under the influence of mollic and gley processes on various soil-forming rocks under conditions of sporadically pulsating water regime and excessive moisture under the meadow, meadow and swamp biocenoses. The ferrum concretions are characteristic of all genetic horizons of mollic gley soils, except for the soil-forming rock, and their content ranges from 3.3% in O to 47.1% in the ABg horizon. The size of the ferrum concretions forms fractions increases with depth. If in the O horizon the maximum size of ferrum concretions is 2.5 cm, then in the ABg it is 7.2 cm.

The gross iron content in the fine mollic gley soils, as well as in the ferrum concretions forms, increases with depth, and the maximum values are characteristic of the ABg horizon and can be explained by the ripple soil water regime, in particular the most frequent annual changes of the groundwater level is typical for ABg horizon, at the same time the upper horizons are rarely affected by mentioned processes. Such changes in the level of groundwater causes the formation of ferrum concretions with a high content of gross iron (Duchaufour and Sochiers 1978, Vodinaskij 2002, Jaworska *et al.* 2016). The lowest values of the gross iron content are characteristic of the fine soil-forming rock (16.0 mg / 100 g soil) and the mollic soil (66.4 mg / 100 g soil). In the ferrum concretions forms, the gross iron content is relatively large, and its maximum value (233.6 mg / 100 g soil) is characteristic of the ferrum concretions of the ABg horizon, which allows us to assume an increase in the gross iron content with an increase of the ferrum concretions fractions in size.

The gross chemical content of the ferrum concretions forms is dominated by the iron oxides with the highest content in the ferrum concretions of the mollic soils (48.75%). The iron oxides in the ferrum concretions slightly decreases

to 41.7% with the depth. Also, the ferrum concretions forms of iron are characterized by a rather high content of aluminum oxides, the content of which decreases with the depth from 7.92% in the ferrum concretions of the O horizon to 5.59% in the ABg one. Silica ( $\text{SiO}_2$ ) with its highest content (96.32%) in the soil-forming rock is dominant in the gross chemical content of the fine mollic gley soils.

The highest values of the accumulation coefficient are characteristic of the iron oxide ( $K_x = 7.21\text{--}2.58$ ), which confirms the hypothesis of the dominant role of its compounds in the formation of the ferrum concretions forms. The relative accumulation of calcium ( $K_x = 1.94\text{--}3.13$ ) is characteristic of the upper humus horizons due to the biological circulation of this element under the meadow biocenoses.

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