

**Ecological and geochemical assessment of the content of chemical elements
and features of their spatial distribution in Fe nodules of soils
in the Middle Cis-Urals**

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Abstract

This work is about the ecological and geochemical assessment of the elemental chemical composition of soil nodules in the taiga zone of the Middle Cis-Urals. The features of the spatial distribution of chemical elements in concretions of Umbric Albeluvisols Abruptic, Luvic Stagnosols Dystric, and Haplic Fluvisols Oxyaquic are characterized for the first time using atomic absorption spectrometry and scanning electron microscopy with energy-dispersive analysis. A concentric ring structure of nodules with alternating zones rich in Fe and Mn has been revealed. Nodules act as geochemical barriers and accumulate not only iron and manganese, but also Cu, Ni, Co, Zn, and Pb.

Keywords: ALBELUVISOLS, STAGNOSOLS, FLUVISOLS, ORTSHTEIN, ROENSTEIN, GEOCHEMISTRY CONSTANTS, ATOMIC ABSORPTION SPECTROMETRY, SEM/EDS, FE AND MN DISTRIBUTION, RING MICROSTRUCTURE

Introduction

Ferromanganese nodules (*FMN*) form in soils of humid landscapes [1–4]. The *FMN* contain information about soil processes and geochemistry of elements [5–8].

The formation of the *FMN* is the main form of deposition of Fe and Mn oxides in soils. This is the most efficient and long-term process of metal binding in soils. Nodules are formed during the alternation of oxidizing and reducing phases of soil formation. Geneis of concretion reduces the availability of contaminant metals. Nodules are a geochemical barrier to many potentially toxic chemical elements. [4, 9–15].

The relevance of studying the processes of accumulation of heavy metals (*HM*) in the nodules is determined by the enrichment in the *HM* of parent rocks and soils, variable

redox conditions of soil formation on the eastern part of the Russian Plain (Middle Cis-Urals) [1, 3, 16] and a high technogenic load on the environment of the region [17–24].

Genesis and geochemical features of nodules. The *FMN* are formed in soils of regions with common climate characteristics: heavy rainfall, low evaporation, long duration of soil freezing in winter and thawing of soil in spring, as well as repeated freezing [25, 26].

The formation of the *FMN* occurs due to cyclic changes in the redox state of soils [27], with the participation of the processes of podzolization and gleying [28], and the activity of iron-reducing microorganisms [29]. F.R. Zaidelman et al. [30] established in a model experiment that the *FMN* are formed in one to two years.

Z.H. Sun et al. [31] identify three stages of the *FMN* formation in poorly drained, low organic matter, silty loamy soils (Fragiudalfs) in the loess of southeastern Indiana (USA):

1) cementation of silicate potassium-sodium minerals with large pores occurs under the influence of mainly Fe oxides in the soil matrix in a wet state, and the formation of a nodule core;

2) with a strong drying of the soil, the body of the concretion is enriched in Mn in the form of concentric layers outside the core;

3) with moderate drying of the soil, concentric layers are enriched with Fe oxides. According to Z.H. Sun [31], the alternation of zones rich in Fe and Mn in a concentric structure indicates that oxidation and reduction processes often occurred during the formation of nodules.

P. Sipos et al. [32] came to the conclusion that the leading processes of the formation of the *FMN* in Gleyic Fluvisol are the formation of the outer shell and the impregnation of internal parts of the body of nodules with Fe oxides. The authors identified four stages of nodule formation:

1) cementation of large soil particles with Fe and Mn oxides with the formation of irregularly shaped aggregates;

2) formation of the outer band;

3) slow precipitation of iron and manganese oxides in the form of concentric bands;

4) peeling of the outer band from the inner layer [32].

The *FMN* accumulate amorphous Fe in soils with a contrasting stagnant–percolate water regime: dark-gray, dark-gray contact-gley and soddy-podzolic contact-gley soil on dual-layer deposits in the southern part of the East European Plain (Tambov Region). The ratio of acid-

soluble (0.1 N H₂SO₄) forms of Fe and Mn in the composition of concretions increases in the series from dark-gray contact-gley soil to soddy-podzolic contact-gley soil [33].

It is known that minerals Fe and Mn in the composition of the *FMN* are natural geochemical barriers for heavy metals [10, 34].

In Stagnic Fragic Albeluvisol in the foothills of the Carpathians (Poland), W. Szymanski and M. Skiba [35] found that the maximum content of the *FMN* is characteristic of the eluvial horizon Eg and ranges from 7.71% to 27.41% of the mass of the entire soil in the horizon. The chemical composition of nodules from these soils was dominated by: Fe₂O₃ 22.7-41.9%; MnO 2.7-5.4% and AlO 11.7-15.8%. The concentration of other chemical elements was also higher than the surrounding soil material: 1.29% TiO; 0.06% CoO; 0.06% NiO; 0.66% CuO; 0.66% ZnO.

In the *FMN* in the brown forest soils of the Pacific coast of Russia (Primorsky Krai), the concentration of Mn is 10-40 times higher, Co is 5-30 times higher, and Ni is 3-17 times higher than in the soil. The content of Zn in nodules of brown forest soils is at the level of soil [36]. In meadow-brown and brown forest soils in the south of the Russian Far East (Primorsky Krai), the *FMN* intensively accumulate Mn, Co, Pb, and Ni and, to a lesser extent – Cu, Cr, and Mo [10].

The *FMN* accumulate Cd, Pb, Co, and Mo in arable deeply gleyed light gray soils in the southern part of the East European Plain (Tambov Region). The content of Zn and Cu in concretions of light gray soils is significantly lower than in concretions of soddy-podzolic soils of the taiga zone [37].

The *FMN* are significantly enriched in Mn, Pb, Ni, Cu and Zn compared to the soil matrix of a typical Plinthudult in East China [38]. In the *FMN* formed in the Terra rossa of the Yunnan-Guizhou Highlands (Guizhou Province, China), the content of Cd exceeds the background by 268.13 times; Pb – 39.46; Cr – 11.80; Zn – 8.43; Ni – 6.16; Cu – 3.65 times [39]. In the arable Cutanic Luvisol in the southwestern part of the African continent (Namibia), the *FMN* accumulate: Cd 6.83; Zn 137; Cu 45; Pb 597 ppm, which is higher than the clarks of these elements [8].

In the alluvial meadow soils of the Bolshaya Kokshaga Natural Reserve in the east of the East European Plain (the Republic of Mari El), the *FMN* contain Mn 30 times higher than in the surrounding soil, Ba – 11 times, P, Ni, Zn, As, Fe, and S – more than two times [40].

The interior of nodules is an important basis for conclusions about soil processes and the ecological state of the environment [5, 10, 41–43]. The features of the internal structure and spatial distribution of chemical elements in the *FMN* were studied in the subtropical Typic Plinthudult formed on Quaternary red-colored rocks of East China. [38]. The studied Fe-Mn nodules are composed of quartz, muscovite, and kaolinite. The presence of quartz and kaolinite suggests authigenic formation of concretions, probably as a result of impregnation and cementation of the soil matrix with Fe and Mn oxides. The total Fe content decreases with increasing nodule size, while the total Mn content, on the contrary, increases. The content of mobile Fe oxides varies from 73 to 75% of the total Fe, and mobile Mn oxides is about 96% of the total Mn content. It has been established that Pb is mainly associated with Fe oxides, while Cu, Ni, Cd, and Zn are mainly associated with Mn oxides [38].

The elemental chemical composition of the *FMN* in soils of the Middle Cis-Urals was studied by Yu.N. Vodyanitsky, A.A. Vasiliev and etc. [1, 4, 11, 12, 44, 45]. The concentration of the *HM* and As in the composition of the *FMN* in soils of the region varies in a wide range: Zn 59-139, As 14-75, Cr 34-246, Ni 95-492, Cu 23-134, Mn 465-41433 ppm. It depends on the genesis soils and rocks, redox regimes of soils, the degree of anthropogenic load on the soil cover of the studied landscapes [4, 41].

Despite extensive studies on the study of the elemental chemical composition of Fe-Mn nodules in the soil of the Middle Cis-Urals, information on the distribution of chemical elements in the internal space of these concretions is limited [4] and is often conjectural character [20, 42].

The purpose of the research is the ecological and geochemical assessment of the elemental chemical composition of the *FMN* (1); revealing the features of the spatial distribution of chemical elements in the body of the *FMN* (2).

For this study we chose soils, which are characterized by alternation of restorative phases of temporary excessive moisture providing mobilization and migration of Fe and Mn ions, and subsequent phases of oxidation, when metals are deposited in pores, on the surface of primary soil minerals, as part of biogenic fragments (roots, stems plants, etc.).

Materials and methods

The objects of study were from two soils zones of the Perm region: 1st zone – the area with the heavy loamy Umbric Albeluvisols Abruptic and Rendzic Leptosols Eutric; 2nd zone –

the area of the heavy loamy Umbric Albeluvisols Abruptic (Fig. 1) [46]. Emissions from industrial enterprises affect the survey area, which is located in the zone of influence of the Perm-Krasnokamsk agglomeration [24].

Pit 1-Ch-z is classified as heavy loamy, Umbric Albeluvisols Abruptic. Pedon was formed on eluvial-deluvial deposits. The pit was laid on a gentle slope of southeastern exposure in the vicinity of SNT Cheremshanka, Mostovaya village. Coordinates: 57° 82' 86" N, 56° 51' 12" E. The soil has been in a fallow state for more than 20 years. Humidification of soil is atmospheric, short-term excessive.

Pit 1-S. Luvic Stagnosols Dystric was formed on eluvial-deluvial deposits. Soil belongs to clay varieties by granulometry. The pit was laid down in a low watershed plateau on the southern outskirts of the city of Perm. Coordinates 57° 95' 14" N, 56° 29' 51" E. Type of land is an unused pasture. Humidification of soil is atmospheric, temporarily excessive, with periodic formation of perched water.

Pit 1-N. Haplic Fluvisols Oxyaquic is formed on recent alluvium. Soil granulometry is heavy loamy. The site for laying the pit is the central floodplain on the right bank of the Syn river in the vicinity of the village of Lugovaya, Nytvensky district. Coordinates: 58° 26' 64" N, 55° 59' 78" E. Type of land is a hay. Humidification of soil is atmospheric, short-term, temporarily excessive.

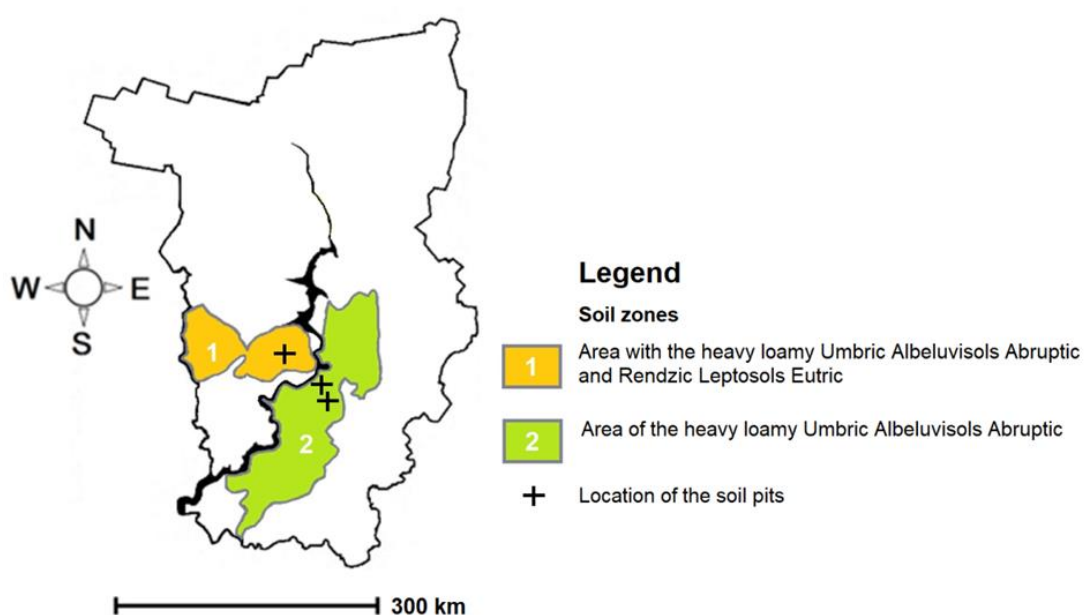


Fig. 1. Location of research objects on the map of soil regions of the Perm Krai according to N.Ya. Korotaev [46]

Research methods

Establishment of soil sections, morphological description of the soil profile and soil sampling were carried out in accordance with the methods of large-scale soil surveys [47]. Nodules were separated from the fine soil ($d > 1.0$ mm) by wet sieving method.

The exchange acidity of the soil was determined by the method of TsINAO (1 H KCl at soil = 1: 2.5). The content organic carbon was determined using the Turin method. The sum of exchange bases was determined by the Kappen-Hillkowitz method. The granulometric composition of the soil was determined by the Kachinsky pyrophosphate method [47].

The total chemical composition of the soil and nodules was analyzed by atomic absorption spectrometry (AAS). A sample weighing 0.2-0.4 g with an accuracy of 10^{-4} grams was decomposed with 5 ml of a mixture of concentrated nitric and hydrochloric acids (1:3). The AAS samples were carried out in triplicate on an iCE 3500 instrument with flame atomization (Thermo Scientific, USA).

To prepare nodule samples for electron microprobe analysis, they were filled with epoxy resin, polished sections with a cross section of nodules were made with a diamond saw blade, and their surface was polished. Polished surfaces were covered with carbon tape for electron microanalysis. Electron probe microanalysis of nodules was performed using an FEI Quanta 650FEG high resolution scanning electron microscope (FEI, USA) with an EDAX Octane Elite energy dispersive spectrometer. The study of polished sections was carried out in a low vacuum mode at a chamber pressure of 200 Pa and an accelerating voltage of 20 kV.

Energy-dispersive microanalysis was used to obtain maps of chemical elements on transverse sections of undestroyed nodules. Point electron microprobe analysis was used to study the spatial distribution of chemical elements in individual nodules according (Table 1) to 38 energy-dispersive spectra.

The ecological and geochemical assessment of the elemental chemical composition of nodules was carried out using the accumulation-dispersion coefficients (Table 2): KK_{SOIL} , $KK_{BEDROCK}$, CF, and $KK_{VINOGRADOV}$, which were calculated using the following formulas:

Concentration factor relative to soil composition before nodule extraction (KK_{SOIL}):

$$KK_{SOIL} = \frac{C}{C_{SOIL}} \quad (1)$$

C_1 – concentration of the i -th chemical element in nodules, ppm;

C_{SOIL} – concentration of the i -th chemical element in the soil before extraction of nodules, ppm.

Concentration factor relative to bedrock ($KK_{BEDROCK}$):

$$KK_{BEDROCK} = \frac{C}{C_{BEDROCK}} \quad (2)$$

C – concentration of the i -th chemical element in the soil component (soil, concretions), ppm;

$C_{BEDROCK}$ – concentration of the i -th chemical element in the bedrock, ppm.

The KK_{SOIL} value was estimated as follows: if $KK_{SOIL} \geq 1$, then the nodules are enriched in the i -th chemical element. When $KK_{SOIL} < 1$, then the nodules are depleted in the i -th chemical element.

The concentration coefficient relative to the clarke of the lithosphere according to A.P. Vinogradov ($KK_{LITHOSPHERE}$) [48]:

$$KK_{LITHOSPHERE} = \frac{C}{C_{LITHOSPHERE}} \quad (3)$$

$C_{LITHOSPHERE}$ – clarke of the i -th chemical element of the lithosphere according to A.P. Vinogradov [48], ppm.

Contamination factor (CF) [49]:

$$CF = \frac{C}{C_{BACKGROUND}} \quad (4)$$

$C_{BACKGROUND}$ – concentration of the i -th chemical element of the background according to I.S. Kopylov [23], ppm .

Concentration coefficient relative to clarke of world soils according to A.P. Vinogradov ($KK_{VINOGRADOV}$) [50]:

$$KK_{VINOGRADOV} = \frac{C}{C_{VINOGRADOV}} \quad (5)$$

$C_{VINOGRADOV}$ – clarke of the i -th chemical element of the soils of the world according to A.P. Vinogradov [50], ppm.

When using $KK_{LITHOSPHERE}$, CF, and $KK_{VINOGRADOV}$ soil pollution was classified as follows: $x < 1$ “low contamination”, $1 \leq x < 3$ “moderate contamination”, $3 \leq x < 6$ “considerable contamination”, $x > 6$ “very high contamination” [49].

Statistical processing of the research results was carried out in the MS Office 2010 software package according to E. A. Dmitriev [51].

Results and discussion

The physicochemical properties of the Haplic Fluvisols Oxyaquic were as follows: the organic carbon content is medium (2.5%), sum of exchange bases is very high (49.6 cmolc/kg), and exchangeable soil acidity is neutral (pH=7.1). The Luvic Stagnosols Dystric had a low organic carbon content (1.6%), a low amount of sum of exchange bases (9.7 cmolc/kg), and a strongly acid reaction of the exchangeable soil acidity (pH=4.3). The Umbric Albeluvisols Abruptic is characterized by a low content of organic carbon content (1.3%), an average amount of sum of exchange bases (11.0 cmolc/kg) and a strongly acid reaction of the exchangeable soil acidity (pH=4.5).

The Haplic Fluvisols Oxyaquic contained concretion tubes or rorensteins. These nodules had a cylindrical shape with a through channel along the axis, the size was from 5 to 30 mm. The color of rorensteins is brown-ocher and rusty-brown, due to the biochemical and microbiological precipitation of iron compounds from the soil solution on the surface of dead root bodies. The cross section of rorensteins has a concentric structure, which reflects the periodicity of development and the relatively slow rate of formation of nodules under dynamic redox conditions in floodplain soils.

Spherical concretions or ortsteins were formed in the Luvic Stagnosols Dystric and Umbric Albeluvisols Abruptic. The color of the ortsteins is brown-ocher and rusty-brown like that of rorensteins. The size of nodules is from 0.25 to 2.0 mm. In the Luvic Stagnosols Dystric, the AY horizon contained nodules 7.4% of the horizon mass, and in the Eg horizon almost two times less – 4.6% of the horizon mass. The content of concretions in the AY horizon of the Umbric Albeluvisols Abruptic was 2.7% of the horizon mass.

The concentrations of the *HM* and Fe in soils and concretions differ (Table 1).

The gray-humus and podzolic horizons of the Luvic Stagnosols Dystric with signs of gleying (pit 1-S) are depleted in Cu, Ni, Zn, and Fe. The content of Co is estimated as increased relative to the clarke for the soils of the world. The AY horizon is enriched in Mn and Pb relative to the parent rock.

The gray-humus horizon of the Umbric Albeluvisols Abruptic (pit 1-Ch-z) is enriched in Co and Zn, in relation to all used geochemical constants. The horizon is characterized by an increased content of Ni relative to the regional background, as well as Mn relative to the parent rock and clarke for soils of the world. Weak contamination of the Umbric Albeluvisols Abruptic

with Co and Zn is probably due to the activity of machine-building enterprises and thermal power plants located on the southern outskirts of Perm.

Table 1. Content of chemical elements in soils and nodules, values of geochemical constants, ppm (n = 3)

Horizon, depth, cm	Sample	Fe	Mn	Cu	Ni	Co	Zn	Pb
Pit 1-S. Luvic Stagnosols Dystric								
AY, 5-15	soil	9685.00	4322.17	20.13	21.38	11.32	42.14	18.24
	concretions	32251.96	7808.53	22.12	23.34	122.28	58.88	56.26
Eg, 15-30	soil	9898.00	835.81	16.19	19.30	13.07	34.86	8.72
	concretions	38738.32	10249.00	75.93	40.02	244.33	42.54	55.03
BT, 40-70	soil	15557.00	505.45	30.56	41.16	11.50	36.32	12.11
Pit 1-Ch-z. Umbric Albeluvisols Abruptic								
AY, 2-29	soil	11850.82	925.58	28.35	39.89	21.29	99.35	0.00
	concretions	48034.08	2686.60	74.91	94.62	376.89	476.18	0.00
C, 100-110	soil	25405.72	364.29	53.50	59.45	15.22	36.52	0.00
Clarke of the lithosphere		46500	1000	47	58	18	83	16
Clarke of world soils		38000	850	20	40	8	50	10
Background		-	900	50	35	17	70	22

Note: "-" means no data

Table 2. Accumulation-dispersion coefficients of chemical elements (KK) and contamination factor (CF) for soils, according to atomic absorption spectrometry data

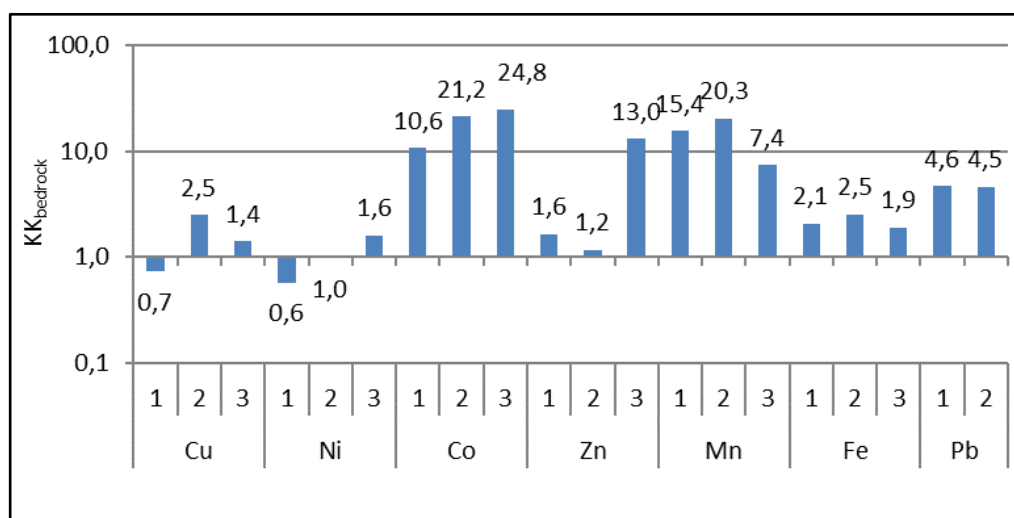
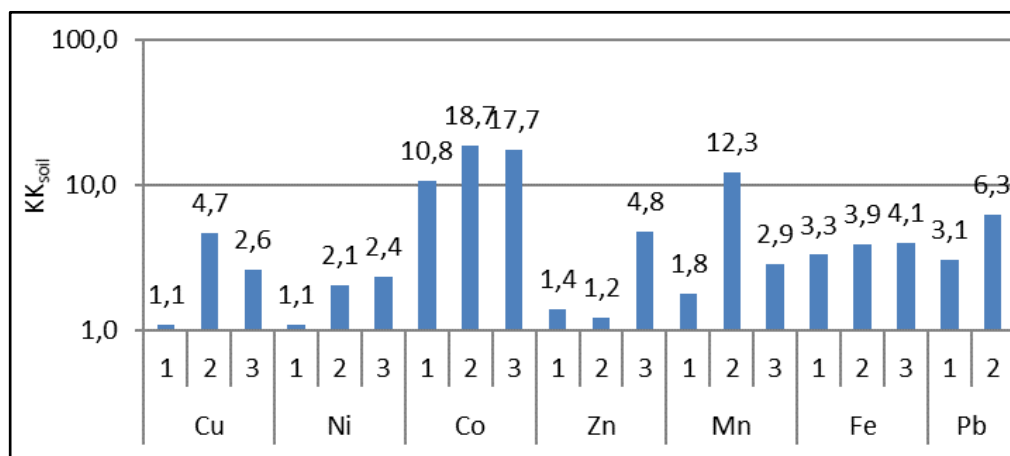
Horizon, depth, cm	Indicator	Fe	Mn	Cu	Ni	Co	Zn	Pb
Pit 1-S. Luvic Stagnosols Dystric								
AY, 5-15	KK _{BEDROCK}	0,5	1,7	0,5	0,5	0,9	0,9	1,5
	KK _{LITHOSPHERE}	0,2	0,8	0,4	0,4	0,6	0,5	1,1
	CF	-	0,9	0,4	0,6	0,7	0,6	0,8
	KK _{VINOGRADOV}	0,3	1,0	0,9	0,5	1,4	0,8	1,8
Eg, 15-30	KK _{BEDROCK}	0,5	1,0	0,4	0,5	1,0	0,6	0,7
	KK _{LITHOSPHERE}	0,2	0,5	0,3	0,3	0,7	0,3	0,5
	CF	-	0,5	0,3	0,6	0,8	0,4	0,4
	KK _{VINOGRADOV}	0,3	0,6	0,8	0,5	1,6	0,6	0,9
Pit 1-Ch-z. Umbric Albeluvisols Abruptic								
AY, 2-29	KK _{BEDROCK}	0,5	2,5	0,5	0,7	1,4	2,7	*
	KK _{LITHOSPHERE}	0,3	0,9	0,6	0,7	1,2	1,2	*
	CF	-	1,0	0,6	1,1	1,3	1,4	*
	KK _{VINOGRADOV}	0,3	1,1	1,4	1,0	2,7	2,0	*

Note: "*" is not valid, because Pb content = 0 ppm

Concretions of the Umbric Albeluvisols Abruptic and Luvic Stagnosols Dystric accumulate Cu, Ni, Co, Zn, Mn, and Pb (Fig. 2).

The coefficients of accumulation-dispersion of heavy metals in the concretions of gray-humus horizons of soils form the following geochemical series.

1. relative to the soil before nodule extraction
 - Luvic Stagnosols Dystric: Co 10,8 > Fe 3,3 > Pb 3,1 > Mn 1,8 > Zn 1,4 > Cu 1,1 > Ni 1,1;
 - Umbric Albeluvisols Abruptic: Co 17,7 > Zn 4,8 > Fe 4,1 > Mn 2,9 > Cu 2,6 > Ni 2,4.
2. relative to the bedrock
 - Luvic Stagnosols Dystric: Mn 15,4 > Co 10,6 > Pb 4,6 > Fe 2,1 > Zn 1,6 > Cu 0,7 > Ni 0,6;
 - Umbric Albeluvisols Abruptic: Co 24,8 > Zn 13,0 > Mn 7,4 > Fe 1,9 > Ni 1,6 > Cu 1,4.



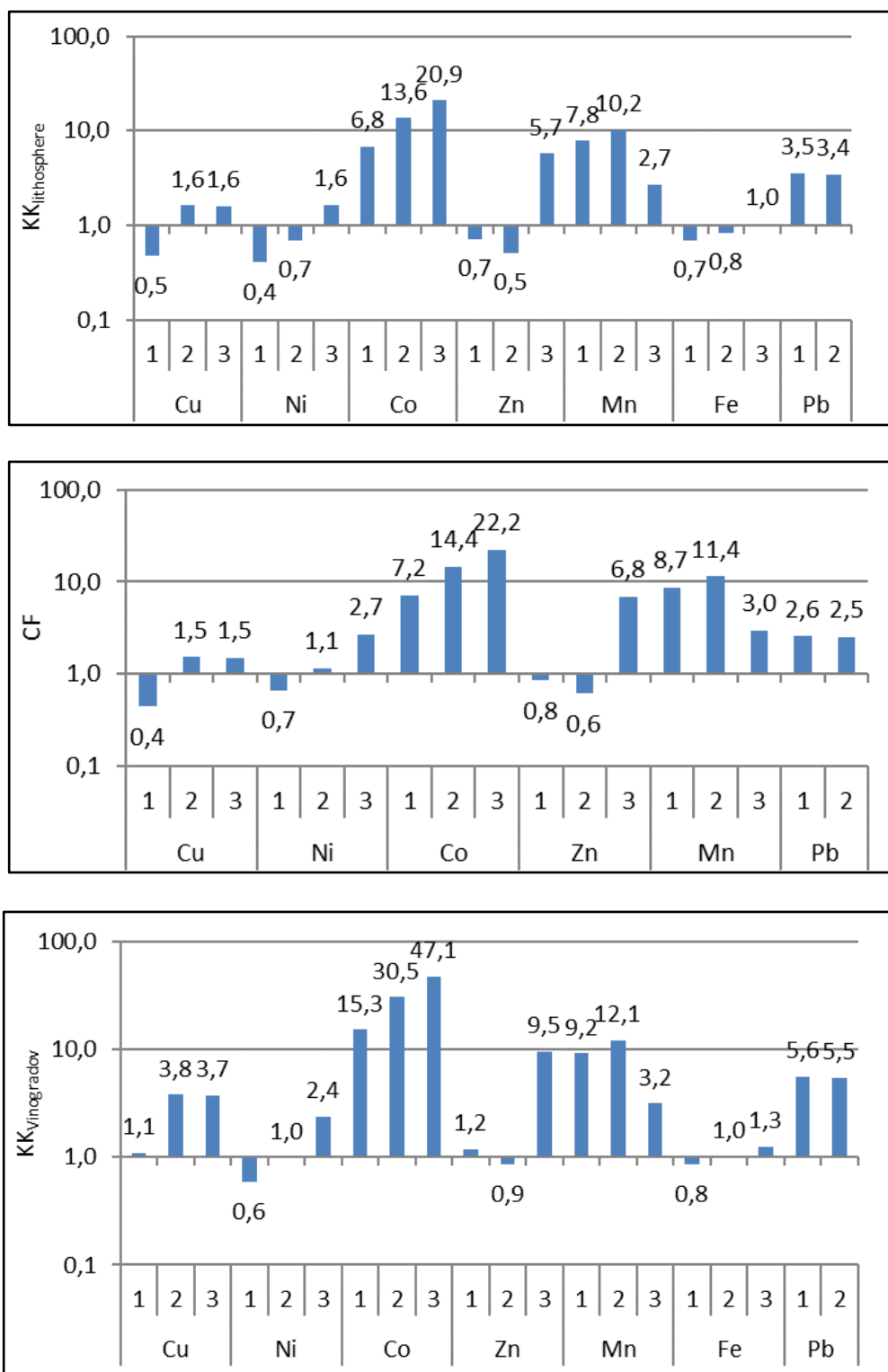


Fig. 2. Accumulation-dispersion coefficients of iron and heavy metals in nodules

Notes: 1 – nodules isolated from sod-shallow podzolic clay superficially peeled soil, section 1-C, horizon AY, 5-15 cm; 2 – nodules isolated from sod-shallow podzolic clay superficially peeled soil, section 1-C, horizon AY, 15-30 cm; 3 – nodules isolated from sod-deep podzolic heavy loamy soil, section 1-H- z, horizon AY, 2-29 cm.

Figures 3A-3C show electron microprobe images in reflected electrons of the surface of thin sections of transverse sections of nodules. The light gray color on cross sections of nodules is due to the presence of iron, manganese, titanium, and heavy metal atoms with a mass of about 50 units or more. Dark gray color on micrographs – zones in which compounds of chemical elements with low atomic mass predominate – carbon, nitrogen, aluminum, silicon, phosphorus, potassium, etc.

The rorenstein formed in the gley horizon of Haplic Fluvisols Oxyaquic (pit 1-N) is distinguished by the preservation of the morphological structure of the root fragment, around which a rhizoconcretion formed due to its replacement and overgrowth. In the center of the inner part of the nodule, there is a well-defined cavity, the inner axial canal of the rorenstein. The inner part of the rorenstein, from the axial channel to the outer shell, is clearly divided by color in the reflected electrons into three layers: the first one has the darkest ring in the center; the second is the largest ring, which has a predominantly light gray color; the third is the thin outer dark ring or sheath of the rhizoconcretion (Fig. 3 A).

A spherical nodule or nodule separated from the gray-humus horizon of the Luvic Stagnosols Dystric has a concentric structure. Three components of the concretion are distinguished: the core, the outer shell and the inner dividing ring. Accumulations of metal compounds with high atomic mass are clearly fixed as a light ring on the surface of the nucleus (Fig. 3 B).

On the transverse section of the nodules from the gray-humus horizon of the Umbric Albeluvisols Abruptic, two parts are distinguished. The first part is a gray core, the second part is a dark gray shell of the core. In the micrograph in the reflected electrons, the gray color of the nucleus and its shell is due to the predominance of atoms of chemical elements with a mass of less than 50 units (Fig. 3 C).

The creation of color ESM/EDS maps of the distribution of chemical elements on cross sections of ferruginous nodules made it possible to clarify the spatial heterogeneity of the elemental chemical composition of neoformations (Fig. 3 D - F).

The rorenstein body is characterized by a well-defined concentric distribution of some chemical elements (Fig. 3 D). Phosphorus and manganese are accumulated in the inner ring of the rhizoconcretion encircling the axial canal of the glandular tubule. At the morphological level, this area consists of cells of the vascular bundles of the plant root. The largest area in the

transverse section of the rhizoconcretion is occupied by an aluminosilicate layer impregnated, possibly, with iron hydroxides. The second manganese-iron layer is the outer shell of the rorenstein. In addition, accumulations of iron compounds of a focal nature were revealed, due to the vital activity of colonies of iron-reducing microorganisms (Fig. 3 D) [29].

The spatial distribution of chemical elements within the body of the ortstein isolated from the gray-humus horizon of the Luvic Stagnosols Dystric is heterogeneous (Fig. 3E). Iron is concentrated in the central part of the ortstein. The ortstein core is the center of concretion formation. Colonies of iron-reducing bacteria initially formed on the surface of a particle of magnetite, maghemite, hematite, or another iron mineral. The body of the ortstein gradually “expanded” due to the ferruginization of the aluminosilicate clay matrix of the soil surrounding the nodule formation center, the growth occurs due to the “sticking” of the soil mass from the enclosing matrix. Manganese (1.3%) forms a well-defined annular framework on the surface of the glandular core within the nodule (Fig. 3 E).

On the distribution map of chemical elements, iron is confined to the periphery of the cross section of the ortstein of Umbric Albeluvisols Abruptic (Fig. 3 F).

The studied nodules and rorensteins are characterized by a general regularity in the spatial distribution of chemical elements: from the center of the concretion to the periphery, the content of iron increases and the content of manganese decreases (Fig. 3 G - I).

The content of iron and manganese in nodules varied: Fe 1.67-19.22%, Mn 0.25-3.71% (Table 3). The concentration of other macroelements in the composition of the aluminosilicate part varied in a wide range: Si 6.57-25.58%, Al 3.97-22.07%, Mg 0.39-1.68%, K 0.38-1.13 %, Ca 0.09-0.65%, Na 0.65-1.14%. Abnormally high content of nitrogen was revealed – 29700 ppm and phosphorus – 900 ppm. This confirms the biogenic nature of nodule formation, i.e., the participation of microbial colonies in the formation of ferruginous nodules [52]. The content of heavy metals and titanium was as follows: Co – up to 700 ppm, Cr – up to 700 ppm, Ti – from 1600 to 39100 ppm.

The local accumulation of Fe, Mn, Cr, Ti, and N was revealed in nodules relative to the regional background and clarke of world soils according to A.P. Vinogradov. The content of magnesium and sodium in some local zones of nodules exceeds the clarke of the soils of the world (Table 4).

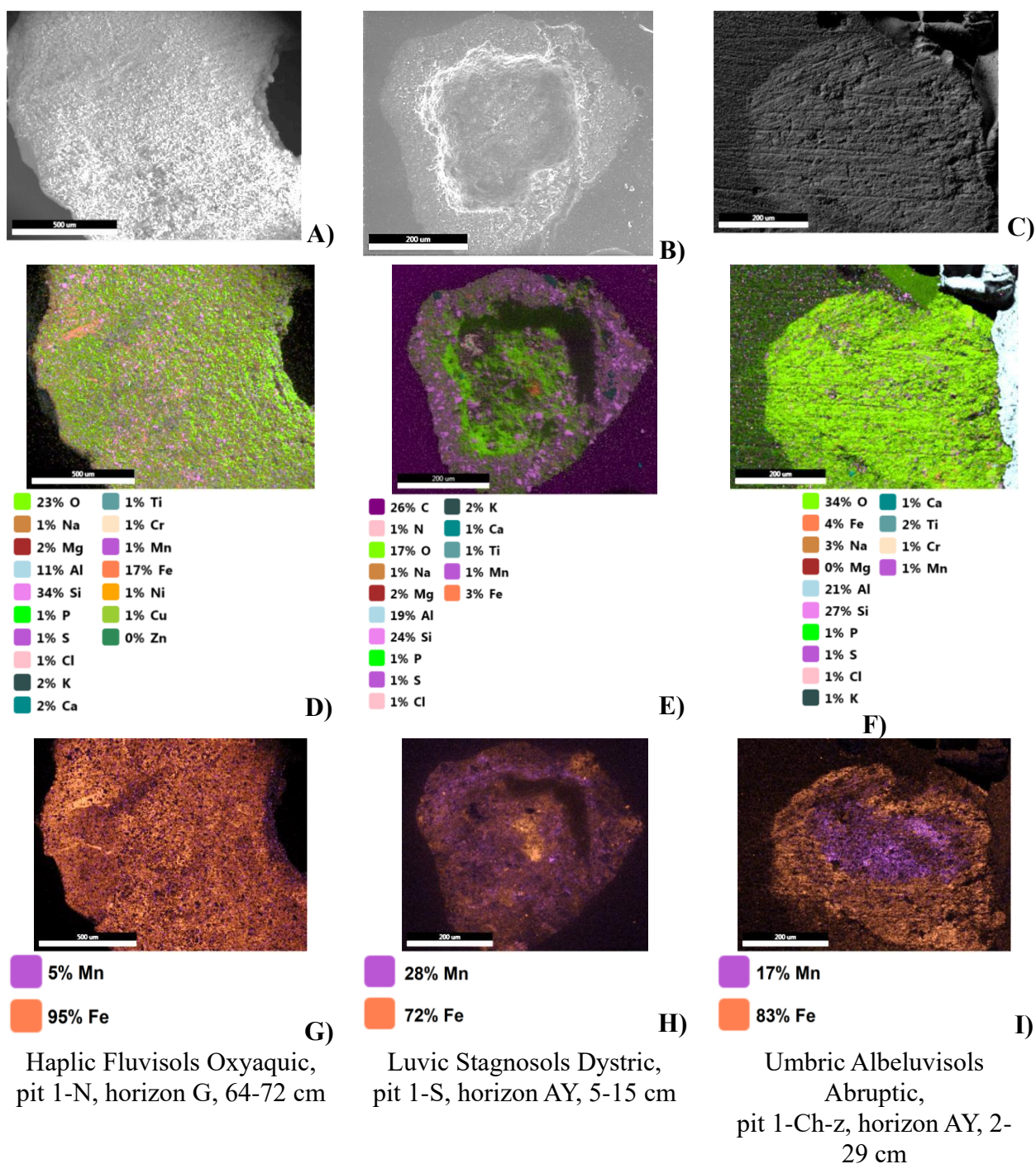


Fig. 3. Results of SEM/EDS analysis of polished sections of nodules in soils of the Middle Cis-Urals: A-C – microimages in reflected electrons; D-F – maps of the spatial distribution of chemical elements; G-I – maps of the spatial distribution of iron and manganese

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Table 3. Elemental chemical composition on sections of undestroyed nodules, according to energy-dispersive analysis data at individual points

Object	Horizon, depth, cm	Number of points, pcs.	O	C	N	Si	Al	Fe	Mn	Ca	Mg	K	Na	P	Ti	Co	Cr
			%														
Pit 1-N. Haplic Fluvisols Oxyaquic	G, 64-72	16	46,79	12,89	*	14,50	3,97	19,22	*	0,09	0,49	0,82	0,84	0,09	0,24	0,07	*
Pit 1-S. Luvic Stagnosols Dystric	AY, 5-15	12	32,95	48,74	2,97	6,57	5,05	1,67	0,25	0,20	0,39	0,38	0,65	0,00	0,16	*	*
Pit 1-Ch-z. Umbric Albeluvisols Abruptic	AY, 2-29	10	35,35	-	*	25,58	22,07	4,66	3,71	0,65	1,68	1,13	1,14	0,04	3,91	*	0,07

Note: "-" – the indicator was not determined; "*" – content below the detection limit.

Table 4. Concentration-scattering coefficients of chemical elements on sections of undestroyed nodules, according to energy-dispersive analysis data at individual points

Object	Horizon, depth, cm	Number of points, pcs.	O	N	Si	Al	Fe	Mn	Ca	Mg	K	Na	P	Ti	Co	Cr
KK_{BACKGROUND}																
Pit 1-N. Haplic Fluvisols Oxyaquic	G, 64-72	16	1,14	-	0,56	0,57	4,75	-	0,03	0,30	0,38	0,39	1,13	0,60	43,73	-
Pit 1-S. Luvic Stagnosols Dystric	AY, 5-15	12	1,37	3049,47	0,43	1,22	0,70	4,88	0,13	0,41	0,30	0,51	0,00	0,69	-	-
Pit 1-Ch-z. Umbric Albeluvisols Abruptic	AY, 2-29	10	0,75	-	0,87	2,74	1,00	37,10	0,22	0,90	0,45	0,46	0,43	8,69	-	8,43
KK_{VINOGRADOV}																
Pit 1-N. Haplic Fluvisols Oxyaquic	G, 64-72	16	-	-	0,50	0,64	5,81	-	0,07	0,90	0,69	1,53	1,31	0,59	98,39	-
Pit 1-S. Luvic Stagnosols Dystric	AY, 5-15	12	-	57,94	0,39	1,38	0,86	5,74	0,28	1,21	0,55	2,01	0,00	0,68	-	-
Pit 1-Ch-z. Umbric Albeluvisols Abruptic	AY, 2-29	10	-	-	0,78	3,10	1,23	43,65	0,47	2,67	0,83	1,81	0,50	8,50	-	3,50

Note: "-" – the content is below the detection limit

Conclusions

Fe nodules are geochemical barriers and accumulate Cu, Ni, Co, Zn, Mn, and Pb in the Haplic Fluvisols Oxyaquic, the Luvic Stagnosols Dystric, and the Umbric Albeluvisols Abruptic. SEM/EDS mapping revealed a concentric ring structure of nodules with alternating phases rich in Fe and Mn. The core of the nodules is enriched in manganese. The ring-centric structure of nodules reflects contrasting redox conditions of soil formation and precipitation of metals in soils of the Middle Cis-Urals under conditions of temporary excess moisture.

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