

Influence of Organic Compounds on Ni, Co, Cu, Cr, and Pb Accumulation by Nodules in Agro-Dark-Humus Podbels (Planosols) in the South of Primorskii Region

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Abstract—The involving of organic compounds in accumulation of Ni, Co, Cu, Cr, and Pb by Fe–Mn nodules in agro-dark-humus podbels (Planosols (Aric)) under different types of long-term agrotechnical impact has been studied in the south of Primorskii region. The profile patterns of the level of SOC content in soils and in nodules indicate the active deposition of organic compounds in nodules in the lower parts of soil profiles in the of fallow and phytomeliorative variants of the experiment. Fulvic acids were noted to predominate in the composition of humus in the nodules in these variants. The long-term application of organic fertilizers contributed to the decrease of SOC incorporation into nodules and to the increase of the part of humic acids in nodules. Nodules were characterized by a high accumulation levels of Co and Pb in all variants of the experiment. Accumulation of Ni, Cr, and Cu was recorded in nodules from particular horizons of studied soils. The intensity of elements accumulation in nodules of different variants of the experiment varied. Accumulation of Ni was controlled by the content of Mn-containing compounds. Based on the analysis of relationships between the contents of SOC, compounds of Fe and Mn, and trace elements, the relative influence of Fe-containing and organic compounds in accumulation of all studied elements by nodules has been identified.

Keywords: Fe-Mn nodules, soil organic compounds, humus type, trace elements, Planosols

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INTRODUCTION

Iron–manganic nodules (IMNs) are the specific soil neoformations, which are distributed in soils of landscapes with changing redox regime in a wide range of bioclimatic zones [6, 15, 27, 32, 33, 47]. Specific character of the structure, composition, and properties of IMNs contributes to the formation of high accumulative capacity of IMNs for elements with variable valence, and this allows considering the IMNs as peculiar geochemical microbarriers in soil profile [16, 19, 25, 29–32, 39, 51–53].

Accumulation of trace elements in IMNs, which are required by living organisms in certain quantities, species, and proportions, is a point of peculiar interest. The increased contents of some trace elements have toxic effects and cause mutagenic and carcinogenic effects [36]. The results of some researches testify to the accumulation of Co, Pb, Cd, Cu, Zn, Cr, and Ni in IMNs and indicate variations of contents and accumulation of elements in IMNs in different soils including soils formed in the zones with different types of technogenic influence [27, 30, 33, 52, 53]. Accumulation of trace elements in IMNs is accompanied by the decrease of their mobility in soils and limiting

their input to soil solution and environmental objects [17, 29, 50, 53, 55, 58].

Amorphous and crystallized in varying degree Fe- and/or Mn-enriched (hydr)oxide compounds are the main phases, which accumulate trace elements in IMNs [25, 39–41, 49, 51, 52]. Trace elements in IMNs are subdivided into two groups according to the level of inter-element interaction: with Mn (Co, Zn) and with Fe (Cr, Pb) [24, 40–42]. The results of some researches indicate the presence of carbon-enriched zones in IMNs [13, 26, 45, 52]. Organic matter of IMNs is composed mostly of stable aromatic groups and is characterized by higher mineralization and age in comparison with organic matter of host soil mass [26, 45]. Organic matter of IMNs is considered in most works as “immobilized inert organic carbon.” The results of our research allowed to affirm that carbon-enriched zones within IMNs represent active centers of accumulation of such elements as Fe and Cu [13, 52]. The obtained data agree with the results presented by the authors [56], in which close correlation was demonstrated between carbon and Mn oxides in IMNs. Taking into consideration the leading role of Fe–Mn-enriched components in accumulation of

trace elements by IMNs and the relationship of such components with organic matter of IMNs, it may be assumed with great probability that organic matter of IMNs participates directly in the formation of accumulative capacity of IMNs. However, the study of these issues didn't receive due attention at present time. Such studies are most actual for soils of agricultural landscapes, where using of different systems of agrotechnical measures adjust the processes of humus and nodule formation, along with the accumulative capacity of IMNs [13, 18, 27]. It is likely that this approach will reflect changes in the group composition and reaction activity of organic matter in IMNs.

Most arable lands in Primorskii region are represented by agro-dark-humus soils with different levels of gley process manifestation, contrast variations of redox regime, and active formation of IMNs in the profile (up to 34.4% of soil weight) [7, 8, 13–15, 18]. Iron–manganic nodules in arable soils of Primorskii region contain up to 90% of total content of Co, 60 to 75% of Mn and Ni, 35 to 47% of Cu, Pb, and Mo, 16 to 20% of Cr in soil, and up to 21% of total soil content of C [13, 18]. The intensity of elements fixation in IMNs affects the ecological state of arable soils, productivity of agroecosystems, and quality of agricultural products [17]. However, the information about the influence of IMNs on depositing of organic carbon, composition and properties of organic matter in IMNs and its influence on accumulation of trace elements in IMNs are very limited.

The aim of our work was to study the influence of organic compounds on the accumulative capacity of IMNs in arable soils for the trace elements and the relationships among trace elements and the main nodule-forming elements.

OBJECTS AND METHODS

To estimate the organic matter content in IMNs and to study its influence on the processes of trace elements accumulation in IMNs, full-profile soil pits were dug on the flat sites in the Rakovka River valley in Ussuriisk district, Primorskii region, on the plots of long-term field experiments performed by the A.K. Chaika Federal Research Center of Agricultural Biotechnology of the Far East. The studied soils were qualified for typical, gleyic, and gley subtypes of agro-dark-humus podbels (Luvic Albic Mollic Planosols (Epiloamic, Endoclayic, Aric)), Luvic Albic Planosols (Loamic, Bathyclayic, Aric), and Gleyic Luvic Albic Planosols (Loamic, Bathyclayic, Aric), respectively [57]. These soils were formed on lacustrine–alluvial deposits of heavy texture [18].

The samples of IMNs and enclosing soil mass were taken in the long-lasting fallow (85 years), phytomeliorative (15 years), and fertilized with half-decomposed cattle manure (62 years) variants of the experiment. Two full-profile soil pits were dug in each vari-

ant of the experiment. Soils of phytomeliorative variant were added to the experiment after removal from the surface of the plot of uncontrolled solid domestic wastes. After ground surface levelling, brome (*Bromus inermis*) was sown during the whole period of phytomeliorative experiment. Soil of the variant with long-term application of organic fertilizer was used in nine-course rotation system. Soil samples were taken after 9 full rotations in the set: wheat–soybean–wheat and sum total application of 240 t/ha manure. Detailed description of climatic conditions in the studied region, positions of soils in the studied variants of the experiment, morphological characteristics, and the main physicochemical properties of soil are presented in the work [14].

The IMNs were isolated from genetic horizons of soils in every variant of the experiment with wet sieving with subsequent separation of nodules from admixtures (adhered mineral particles and organic residues) under laboratory conditions [13, 53]. To carry out the study of chemical composition of IMNs, the samples (about 3000 nodules) were used, the surface of which was preliminarily cleared from small particles of fine earth with the help of 20-min immersion into the ultrasonic bath of alcoholic solution (50%) according to the recommendations [27]. When studying the distribution of elements within IMNs, about 100 samples were fixed in epoxide resin. Subsequently, the epoxide blocks were cut to two equal parts and polished. About 5000 samples of IMNs were used for analyses.

IMNs were carefully removed from host soil mass under laboratory conditions, and the samples of soil mass without IMNs were called “soil” in further presentation of material of research.

Concentrations of macroelements in the samples of IMNs and soils were determined with the method of energy dispersive X-ray fluorescence spectroscopy in analyzer EDX 800HS-P (Shimadzu, Japan), using state standard reference samples (GSO 901-76, 902-76, 903-76, 2498-83, 2499-83, 2500-83, 2507-83, 2509-83) according M-02-0604-2007 [10]. The description of parameters of measuring, format and working environment of analyses are described in the work [14]. Measurement reliability was tested by the analysis of one standard samples after 10 unknown (experimental) samples. Maximal deviation of concentration of trace element from certified value of standard sample in experimental samples did not exceed 0.9%.

Concentrations of Cu, Cr, Pb, Ni, Co in the samples of IMNs and soils were determined by atomic absorption spectrometry on a AA-6800 spectrometer (Shimadzu, Japan) after complete chemical decomposition of analyzed material by the mixture of hydrofluoric (HF) and nitric (HNO₃) acids according to [44]. Analytical quality control was carried out with



Fig. 1. Iron-manganic nodules of different size.

the help of standard samples AACD1, AACO1, AACU1, AANI1, AAPB1, and AAZN1.

The maps of distribution of elements within IMNs were obtained with the help of electron probe microanalysis, using the Electron Probe Microanalyzer JXA-8100, Jeol.

The contents of organic carbon (C_{TO}) in the samples of soils and IMNs were determined with Tyurin's method according to the standard procedure; group composition of humus was determined by the method of Kononova–Bel'chikova [12]. The evaluation of the type of humus in soil and IMNs was carried out according to [11]. Color indices of humic acids of IMNs (E_4/E_6) were determined in pyrophosphate extract of humic acids in spectrophotometer UVmini-1240 (Shimadzu, Japan) at wavelengths 465 (E_4) and 665 (E_6) nm [20].

Modern scientific equipment of Research Equipment Sharing Centers "Biotechnology and Gene Engineering", Federal Scientific Center of the East Asia Terrestrial Biodiversity, Far Eastern Branch of the Russian Academy of Sciences and "Primorskii Analytical Center of Local Element and Isotope Analysis", Far Eastern Geological Institute, Far Eastern Branch of the Russian Academy of Sciences was used in the work.

Enrichment factors (EF) of elements in IMNs demonstrated how many times the intensity of elements accumulation in the nodules exceeded the accumulation of these elements in host soil mass (without nodules); they were calculated according to the formula recommended in [29]: $EF = C_{nod}/C_{soil}$, where C_{nod} and C_{soil} are concentrations of particular element in the nodules and soil (without nodules).

Analysis of every parameter in particular experimental sample was carried out in triplicate. Mathematical treatment of obtained data (calculations of arithmetic mean values and mean-square deviations, and correlation analysis) was carried out using the programs Statistica and Microsoft Excel 2007. The difference was considered to be statistically significant at $p \leq 0.05$. The degree of correlation was evaluated according to gradation recommended in [5].

RESULTS AND DISCUSSION

According to classification of soil neoformations, studied IMNs belong to the types of coarse and fine brown nodules [6]. The size of isolated IMNs ranged from 1 to 13 mm (Fig. 1). Most nodules (75%) were represented by the fraction of 3–6 mm. The study of IMN structure demonstrated the presence of outer and internal zones, which differed in density, color, and chemical composition (Figs. 2a and 2c). Outer zone of IMN was characterized by a greater density in comparison with the internal one, brown and ochreous-brown color, and predominance of Fe-enriched compounds. Internal zone had a looser structure, dark brown up to black color, and contained more Mn-enriched compounds. The nodules with such structure and differentiation of Fe and Mn were found in different soils in the south of Far East [13, 16, 52, 53].

A detailed analysis of qualitative distribution of IMNs in soil profiles in the studied variants of the experiment was presented earlier [14]. It should be noted that abundance of IMNs decreased in the series of soils: typical agro-dark-humus podbel (fallow) > gleyic agro-dark-humus podbel (phytomeliorative experiment) > gleyed agro-dark-humus podbel (an experiment with application of organic fertilizer). A decrease in the content of IMNs in this series was mainly due to the increasing hydromorphism and more active gleyzation (reduction processes) preventing crystallization of Fe and Mn compounds in the soil.

The contents of C_{TO} in IMNs from the upper soil horizons at different variants of the experiment varied from 0.78 to 2.74% and generally corresponded to the contents of C_{TO} in the host soil mass (Table 1). Specific features of humus formation and the difference in humus contents in soils the variants of the experiment were presented earlier [14]. It should be noted within the framework of present study that maximal level of C_{TO} content was typical for IMNs of fallow soil. Lower values of C_{TO} were observed in IMNs of soils in the variant of the experiment with long-term application of organic fertilizer. Minimal values of C_{TO} in IMNs

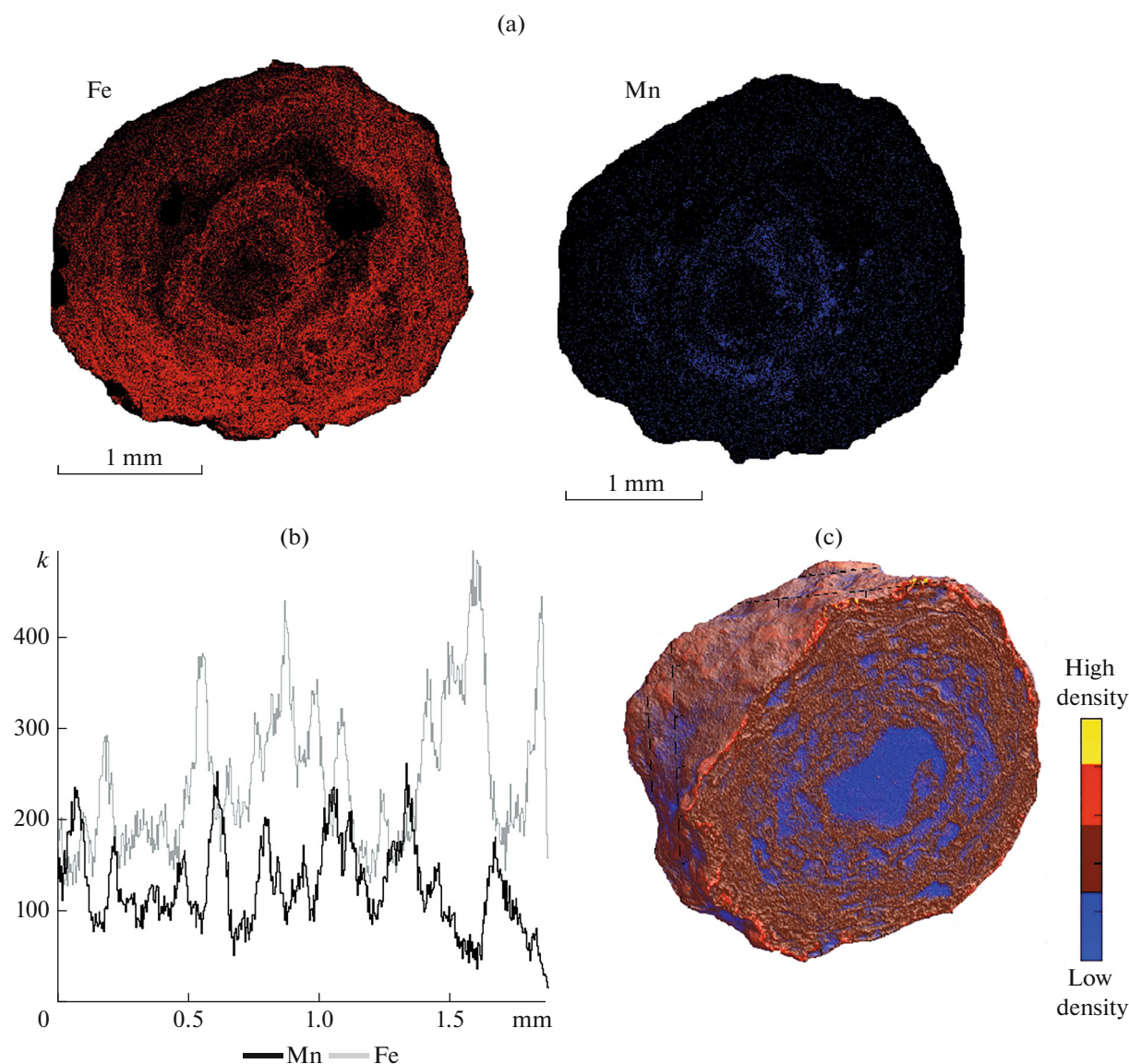


Fig. 2. Distribution of the main nodule-forming elements and the structure of nodules in agro-dark-humus pobbels: (a) maps of Fe and Mn distribution in nodules, (b) changes in Fe and Mn concentrations as a result of deposition in nodules, and (c) structure of nodules.

were found in the samples taken in soils of phytomeliorative variant.

The decrease of C_{TO} content down the soil profile was observed in the samples of soils and IMNs in all studied variants of the experiment. Some works reported active accumulation of carbon in IMNs (*EF* 3.5 to 31) [13, 26, 45]. However, studied IMNs, formed in the upper part of the soil profile in all variants of the experiment (horizons PU and PU–ELnn(g)), were characterized by lower content of C_{TO} and, respectively, humus in comparison with host soil. On the contrary, accumulation of C_{TO} or similar concentrations of C_{TO} in IMNs and host soil were observed in IMNs formed in the lower part of soil pro-

file. Accumulation of C_{TO} (*EF* 16) in IMNs formed in the ELnn horizon is a distinctive feature of IMNs in soils of fallow variant. This horizon is the zone of active formation of IMNs and is characterized by maximum abundance of these neoformation with high percentage of coarse IMNs [14]. Sharp decrease of C_{TO} content in host soil was observed in this horizon. Such sharp decrease of C_{TO} content in the middle part of soil profile is typical for soils of natural landscapes of the region, in which the eluviation process in medium horizon is more pronounced in comparison with their arable analogs and indicates the increase of significance of IMNs in deposition of C_{TO} in soils with similar type of soil formation.

Table 1. Concentrations of C_{TO} and humus composition of host soils and nodules (IMNs), mean arithmetic value \pm standard deviation

Horizon	Depth, cm	Object	C_{TO} , %	C_{ha}	C_{fa}	Nonhydro-lyzable residue	C_{ha}/C_{fa}
				% of C_{TO}			
Typical agro-dark-humus podbel (fallow)							
PU	4–11	Soil	3.18 ± 0.13	21.1 ± 1.0	11.9 ± 0.54	67.0 ± 1.90	1.77
		IMN	2.74 ± 0.10	12.0 ± 0.40	10.6 ± 0.49	77.4 ± 3.20	1.13
PU–ELnn	11–35	Soil	2.40 ± 0.03	18.3 ± 0.80	14.6 ± 0.63	67.1 ± 3.00	1.25
		IMN	1.03 ± 0.01	25.2 ± 1.20	33.0 ± 1.50	41.8 ± 1.99	0.76
ELnn	35–55	Soil	0.05 ± 0.001	–	–	–	–
		IMN	0.80 ± 0.03	8.7 ± 0.29	35.0 ± 1.20	56.2 ± 1.40	0.25
BTnn	55–111	Soil	0.12 ± 0.002	–	–	–	–
		IMN	0.14 ± 0.003	–	–	–	–
Gleyic agro-dark-humus podbel (phytomeliorative experiment)							
PU	0–11	Soil	2.04 ± 0.10	14.7 ± 0.50	15.7 ± 0.50	69.6 ± 2.20	0.94
		IMN	0.78 ± 0.03	14.1 ± 0.49	14.1 ± 0.59	71.8 ± 3.00	1.00
PU–ELnn	11–27	Soil	1.56 ± 0.06	24.3 ± 1.11	16.3 ± 0.70	59.0 ± 2.00	1.49
		IMN	0.66 ± 0.03	12.1 ± 0.38	13.6 ± 0.30	74.3 ± 3.05	0.89
ELnn	27–49	Soil	0.84 ± 0.04	14.3 ± 0.59	22.6 ± 0.90	63.1 ± 2.10	0.63
		IMN	0.44 ± 0.02	11.4 ± 0.50	22.8 ± 0.98	77.2 ± 3.30	0.50
BTnn,g	49–83	Soil	0.005 ± 0.001	–	–	–	–
		IMN	0.05 ± 0.001	–	–	–	–
Agro-dark-humus gley typical podbel (experiment with application of organic fertilizer)							
PU	0–27	Soil	2.22 ± 0.09	20.3 ± 1.00	18.5 ± 0.50	61.2 ± 2.50	1.10
		IMN	1.30 ± 0.05	10.8 ± 0.44	10.8 ± 0.40	78.4 ± 3.40	1.00
ELnn,g	27–42	Soil	2.15 ± 0.08	13.9 ± 0.50	19.1 ± 0.90	62.4 ± 2.63	0.73
		IMN	0.34 ± 0.01	41.2 ± 1.70	20.5 ± 1.00	38.3 ± 1.78	2.00
BTnn,g	42–91	Soil	0.24 ± 0.01	–	–	–	–
		IMN	0.23 ± 0.01	–	–	–	–

Analysis of interactions between the profile pattern of C_{TO} contents in soils and IMNs demonstrated the participation of organic compounds of soil in the process of growth and development of IMNs. Very close correlation was observed in the samples of phytomeliorative and fallow variants of the experiment. Addition of easily decomposable organic residues (fallow and phytomeliorative variants), which are produced by plants, promotes more active incorporation of C_{TO} into IMNs. This is connected first of all with the activation of soil microflora, formation of labile, newly formed, reaction-active organic compounds, and the formation of organo-mineral complexes, including those with the main nodule-forming components (the compounds enriched with Fe and/or Mn). Predominance of highly condensed organic compounds with lower migration mobility and capability for complex

formation (variant with long-term application of organic fertilizer) reflects weakening of relationship between the concentrations of C_{TO} in soils and IMNs.

The main difference between humus composition in IMNs and humus composition of host soils is the predominance of fulvic acids fractions. It is worth to note that the inadequate changes of the humus type in soils and IMNs in different variants of experiment is first of all determined by multiple effects of different agrotechnical procedures on the processes of organic matter transformation in agro-dark-humus pobbels. The group composition of humus in host soils within 4–35 cm (PU and PU–ELnn horizons) changed under the conditions of fallow variant from humate to fulvate-humate. Humus content in the lower horizon (ELnn) was very low, and this made impossible further determination of its group composition. The analysis

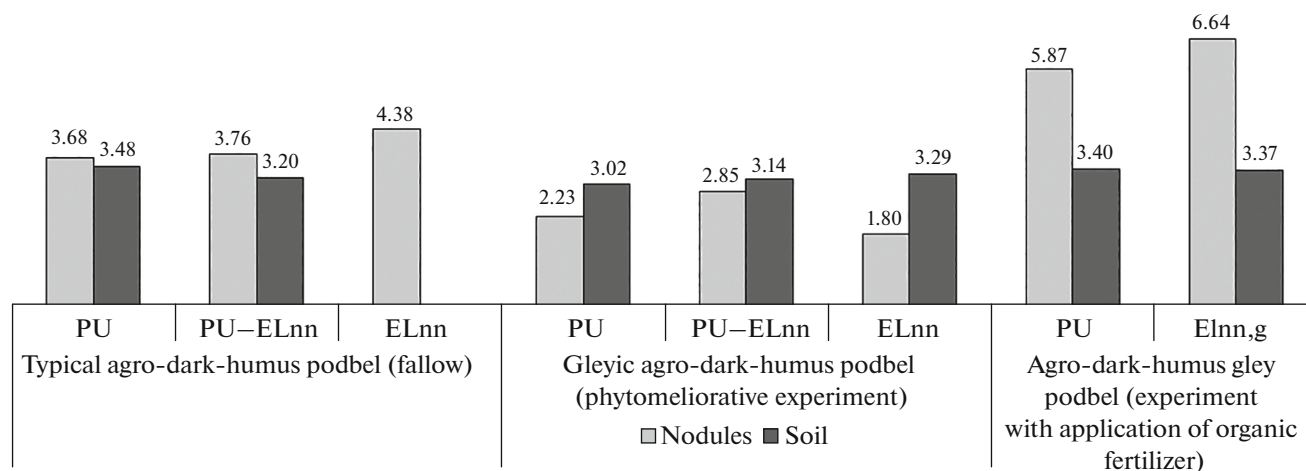


Fig. 3. The values of color index of humic acids (E_4/E_6) in soils and nodules.

of profile changes in group composition of humus in IMNs reflected the trend towards the increase of fulvic acids content in IMNs down soil profile and the change of humus type from fulvate-humate to humate-fulvate and very fulvate. Similar regularity in profile change of group composition of humus was observed in IMNs formed in soils of phytomeliorative variant of the experiment. Low values of C_{ha}/C_{fa} ratio were observed earlier in IMNs of meadow pobbels, which were characterized by the primary role of labile humus compounds in nodule formation [15]. Long-term application of organic fertilizer of animal origin promoted the increase of proportion of humic acids in humus composition of host soils and IMNs. Contrary to IMNs of eluvial horizons in soils of fallow and phytomeliorative variants of the experiment, IMNs of ELnn,g horizon in soils of the variant with long-term application of organic fertilizer had humate type of humus. This probably was connected with periodical migration of humus compounds owing to water-logging and entering of such compounds in IMNs.

Changes in the group composition of humus in soils and IMNs were confirmed by the changes of color index of humic acids (E_4/E_6) (Fig. 3). This index characterizes the system of conjugated double bonds in macromolecules of organic matter and has inverse relationship with their molecular dimensions [20]. Sharp differences in the values of E_4/E_6 parameter were not found in soils of the variants of the experiment. The comparison of the values of E_4/E_6 ratio in IMNs of soils of different variants of the experiment attested to greater molecular dimensions of humic acids in IMNs of soils of fallow and phytomeliorative variants. The decrease of the E_4/E_6 ratio in comparison with host soil was a distinctive feature of humic acids in IMNs of soil of phytomeliorative variant. The increase of E_4/E_6 ratio was observed in IMNs of soils in the variant with long-term application of organic

fertilizer, and this indicated the decrease of molecular dimensions of humic acids. It can be claimed on the basis of differences in E_4/E_6 index that humic acids in IMNs of this variant of the experiment were characterized in comparison with IMNs of soils of fallow and phytomeliorative variants by lower concentrations of hydrogen and nitrogen and increased degree of oxidation and increased number of cyclic structures [1, 9].

To evaluate the influence of C_{TO} on accumulation of trace elements in IMNs, we examined the total contents of Ni, Co, Cu, Cr, and Pb (Table 2). The choice of elements was substantiated by high levels of their accumulation in IMNs of soils in different regions of the world and particularly in IMNs of soils of studied region, and by high values of interaction between selected elements and organic matter in different soils [16, 18, 25, 27, 28, 30, 33, 35, 47, 52, 53]. When comparing the concentrations of trace elements in studied soils with mean values for the world soils [35], we observed increased levels of all studied trace elements, and this reflected the specific character of element composition of soils and parent rocks in the studied region. Regional clarke values were found for major trace elements in arable soils of Primorskii region with due account for the local specificity of soil cover, and this separated them from the world values and allowed more objective evaluating of trace elements concentrations in agro-dark-humus pobbels [4]. The comparison of trace elements concentrations in soils with regional clarke values demonstrated that all the studied soils have a decreased concentration of Ni. Concentrations of Pb in most soil horizons, except for the illuvial ones, are also lower than the regional clarke values; in the illuvial horizons, Pb tends to accumulate, and its concentration exceeds the regional level by 11 to 27%. The exceedance of clarke values in particular horizons was also observed for Co. The concentration of Co in soils varied all over the soil profile with a great amplitude, and the maximum was found in the

Table 2. Concentrations of trace elements in host soils and nodules (IMNs), mean arithmetic value \pm standard deviation, mg/kg

Horizon	Depth, cm	object	Co	Ni	Cu	Cr	Pb
Typical agro-dark-humus podbel (fallow)							
PU	4–11	Soil	36.79 \pm 0.96	41.14 \pm 1.52	42.35 \pm 1.40	79.37 \pm 2.60	27.62 \pm 0.78
		IMN	61.85 \pm 1.73	19.82 \pm 0.54	50.51 \pm 1.96	141.39 \pm 4.93	155.45 \pm 6.60
		EF*	1.68	0.48	1.19	1.96	5.63
PU–ELnn	11–35	Soil	36.59 \pm 0.91	37.05 \pm 1.17	42.04 \pm 1.34	78.82 \pm 2.71	38.01 \pm 1.27
		IMN	62.30 \pm 1.66	14.83 \pm 0.41	45.24 \pm 1.52	126.16 \pm 3.80	120.11 \pm 5.22
		EF	1.70	0.40	1.07	1.60	3.16
ELnn	35–55	Soil	37.41 \pm 1.01	24.80 \pm 0.69	48.16 \pm 1.77	78.56 \pm 2.46	29.97 \pm 1.01
		IMN	56.29 \pm 1.57	23.51 \pm 0.73	79.63 \pm 2.56	140.47 \pm 4.86	177.50 \pm 8.16
		EF	1.50	0.95	1.65	1.79	5.92
BTnn	55–111	Soil	6.53 \pm 0.23	33.19 \pm 1.08	50.20 \pm 1.84	99.83 \pm 3.39	40.69 \pm 1.45
		IMN	41.73 \pm 1.26	35.81 \pm 1.22	18.04 \pm 0.51	108.44 \pm 3.61	291.04 \pm 9.99
		EF	6.39	1.08	0.36	1.08	7.15
BT	111–153	Soil	11.94 \pm 0.39	41.52 \pm 1.47	37.07 \pm 0.75	95.91 \pm 3.28	25.65 \pm 0.67
		IMN	29.55 \pm 0.63	327.34 \pm 9.93	12.51 \pm 0.29	119.91 \pm 3.72	439.00 \pm 15.84
		EF	2.48	7.88	0.34	1.25	17.11
C	153–192	Soil	24.26 \pm 0.55	32.28 \pm 0.96	69.00 \pm 2.15	103.01 \pm 3.59	35.15 \pm 1.08
Gleyic agro-dark-humus podbel (phytomeliorative experiment)							
PU	0–11	Soil	39.77 \pm 1.31	23.12 \pm 0.70	38.85 \pm 1.22	83.93 \pm 3.13	18.53 \pm 0.32
		IMN	68.58 \pm 2.06	29.59 \pm 0.92	32.46 \pm 0.90	97.36 \pm 3.51	96.78 \pm 3.17
		EF	1.72	1.28	0.83	1.16	5.22
PU–ELnn	11–27	Soil	41.24 \pm 1.25	35.42 \pm 1.23	34.68 \pm 0.97	83.70 \pm 3.04	24.24 \pm 0.70
		IMN	79.23 \pm 2.63	34.37 \pm 1.18	12.49 \pm 0.31	93.93 \pm 3.53	82.85 \pm 2.94
		EF	1.92	0.97	0.36	1.12	3.42
ELnn	27–49	Soil	36.13 \pm 0.99	29.61 \pm 0.98	27.75 \pm 0.72	89.29 \pm 3.42	25.55 \pm 0.68
		IMN	98.37 \pm 3.75	27.56 \pm 0.85	16.52 \pm 0.40	82.98 \pm 3.16	85.95 \pm 2.97
		EF	2.72	0.93	0.59	0.92	3.36
BTnn,g	49–83	Soil	10.55 \pm 0.42	31.57 \pm 0.99	43.70 \pm 1.40	103.72 \pm 3.58	28.79 \pm 0.76
		IMN	82.90 \pm 2.77	148.68 \pm 6.92	9.79 \pm 0.28	90.37 \pm 3.19	128.02 \pm 5.54
		EF	7.86	4.71	0.22	0.87	4.45
BTg	83–112	Soil	13.58 \pm 0.51	17.56 \pm 0.41	39.94 \pm 1.27	100.20 \pm 3.62	38.62 \pm 1.12
		IMN	39.40 \pm 1.14	53.54 \pm 2.03	10.61 \pm 0.44	106.61 \pm 3.87	129.75 \pm 5.55
		EF	2.90	3.05	0.26	1.06	3.36
Cg	112–122	Soil	31.05 \pm 0.73	30.31 \pm 0.94	42.22 \pm 1.26	82.66 \pm 2.94	21.90 \pm 0.56
Agro-dark-humus gley podbel (experiment with application of organic fertilizer)							
PU	0–27	Soil	43.80 \pm 1.56	29.29 \pm 0.86	36.77 \pm 1.05	84.52 \pm 3.42	27.12 \pm 0.71
		IMN	123.41 \pm 4.59	22.92 \pm 0.64	44.58 \pm 1.43	178.63 \pm 6.99	131.78 \pm 5.73
		EF	2.81	0.78	1.21	2.11	4.85
ELnn,g	27–42	Soil	42.23 \pm 1.63	46.18 \pm 1.63	41.78 \pm 1.25	83.67 \pm 3.21	15.61 \pm 0.22
		IMN	97.55 \pm 3.47	15.93 \pm 0.47	56.59 \pm 1.80	128.11 \pm 3.90	161.06 \pm 6.01
		EF	2.31	0.34	1.35	1.53	10.32
BTnn,g	42–91	Soil	14.33 \pm 0.58	40.25 \pm 1.33	65.53 \pm 2.40	107.24 \pm 3.51	40.94 \pm 1.43
		IMN	41.36 \pm 1.37	39.01 \pm 1.24	44.78 \pm 1.45	114.75 \pm 3.68	131.36 \pm 5.59
		EF	2.88	0.97	0.68	1.07	3.21
G	91–132	Soil	24.42 \pm 0.70	27.61 \pm 0.79	42.88 \pm 1.29	97.39 \pm 3.16	33.79 \pm 0.94
		IMN	63.55 \pm 1.81	45.28 \pm 1.47	21.70 \pm 0.63	108.53 \pm 3.60	88.01 \pm 3.30
		EF	2.60	1.63	0.50	1.14	2.60
CG	132–170	Soil	25.94 \pm 0.73	35.46 \pm 1.16	61.07 \pm 1.99	107.28 \pm 3.76	22.30 \pm 0.57
Mean content in the world soils, mg/kg [34]			11.3	29.0	38.9	59.5	27
Regional Clarke number in soil, mg/kg [4]			22	46	20	66	32

*EF, enrichment factors of elements in nodules.

upper and middle parts of soil profile, where Co concentrations were 1.6–2 times higher than the regional Clarke. Concentrations of Cu and Cr exceeded the values of regional Clarke by 1.4–3.5 and 1.2–1.6 times, respectively. The results of numerous studies indicated the appearance of signs of suppression of plant growth under increased content of Cu and Cr in soil [2]. However, plants grown on the studied soils were characterized by high yield and phytomass productivity and did not demonstrate any signs of growth disturbance. This was apparently connected with being of most Cu and Cr in tightly bound and not available for plants compounds. Analysis of vertical distribution of Cu and Cr in the soil profile indicated a predominately lithogenic input of these elements in soils. Additionally, profile change of Cu content in soil fine earth in all studied variants of the experiment was characterized by a pronounced eluvial-illuvial distribution. Similar type of vertical distribution was recorded for Ni in soil profiles of fallow and phytomeliorative variants of the experiment. Maximal concentrations of Ni were identified in soils of variant with long-term application of organic fertilizer in the middle part of the soil profile and in the transitional to parent rock horizon.

All studied trace elements were found in IMNs. Analysis of data on the content of trace elements demonstrated variation of concentrations and intensity of accumulation of elements in IMNs of soils in different variants of experiment. The main difference of IMNs of the host soil was a sharp increase of Pb and Co concentrations to the levels exceeded the values of the world and regional Clarkes from 3.1 to 16.3 times for Pb and from 2.6 to 11 times for Co. The IMNs formed in the lower part of soil profile were characterized in comparison with the host soil by the increase of Ni content. Clarke values of Ni content in IMNs in lower horizons were exceeded from 1.4 to 11.3 times. The most active enrichment of nodules with Cu and Cr was observed in the upper and middle parts of soil profiles in fallow and variant with application of organic fertilizer. Maximal exceedance of Clarke concentration of Cr was about 1.5 times in IMNs of soil in variant with long-term application of organic fertilizer and for Cu 4.0 times in IMNs of fallow soil. Concentrations of Ni, Cu, and Cr in IMNs were lower or differed insignificantly from concentrations of elements in soil in all other cases.

Profile differentiation of concentrations of trace elements in IMNs demonstrated similar to soil fine earth type of Co distribution in all variants of the experiment. Vertical distribution of Ni in IMNs soils of fallow and phytomeliorative variants corresponded to their distribution in host soil. Unlike the Ni distribution pattern in soil of variant with application of organic fertilizer, concentrations of the element increased in IMNs of the lower part of soil profile. Vertical distribution of Cu in IMNs and host soil in all variants of the experiment, and Cr in the samples of IMNs and soils in fallow variant and in the variant

with organic fertilizer displayed an inversely proportional relationship, when the decrease of element concentration in soil fine earth was accompanied by the increase of its content in IMN. The profile distribution of Cr in IMNs of phytomeliorative variant indicated the presence of eluvial-illuvial differentiation. Vertical distribution of Pb in IMNs was characterized by the increase of content in neoformations of the lower part of the soil profile in fallow and phytomeliorative variants of experiment. Maximal Pb content in soil IMNs in the variant with organic fertilizer was observed in eluvial horizon against the background of sharp decrease of the element content in soil fine earth of host horizon.

The relationship between concentration and accumulation of trace elements in IMNs and in the host soil is expressed by *EF* value, indicating active accumulation of Co and Pb in IMNs all over the profile of studied soils. Nickel, Cr, and Cu were accumulated in IMNs less intensely. Accumulation of Ni, Cr, and Cu in IMNs was characterized by pronounced profile differentiation with the increase of *EF* in particular horizons of the soil profile. The intensity of Ni and Co accumulation increased in IMNs formed in the lower part of soil profile. More active accumulation of Cr was on the contrary associated with IMNs of humus horizons. Accumulation of Cu was observed in IMNs of soils of fallow variant and variant with organic fertilizer, in which the most intense accumulation of the element was found in eluvial horizon. Maximal level of Pb in IMNs of soils in different variants varied and was associated with the lower part of the soil profile in fallow soil, arable horizon of soil of phytomeliorative variant, and eluvial horizon of soil in the variant with long-term application of organic fertilizer.

The results of research confirmed the inconsistency in the contents of trace elements in soils and IMNs in different variants of the experiment. Insignificant increase of Co and Cr concentrations and decrease of Pb, Ni, and Cu concentrations was observed in arable horizons of soils of phytomeliorative variant and variant with application of organic fertilizer in comparison with fallow variant. The comparison of intensity of accumulation of trace elements in IMNs in soils of different variants of the experiment on the basis of *EF* suggested more intense accumulation of Pb, Ni, and Cu by the nodules of fallow soil. The intensity of Co accumulation increased in IMNs of soil of phytomeliorative variant. IMNs in the arable horizon of soil in the variant with long-term application of organic fertilizer had a high *EF* of Cr.

The differences in concentrations and intensity of accumulation of trace elements in IMNs of soil in different variants of the experiment with the same direction of the main soil-forming process indicated probable activation of different reaction-active phases in IMNs under the influence of different field management. Such phases are presented first of all by Fe-

Table 3. Concentrations of macroelements in host soils and nodules (IMNs) mean arithmetic value \pm standard deviation, mg/kg, %

Horizon	Depth, cm	Object	SiO ₂	Al ₂ O ₃	MgO	TiO ₂	Fe ₂ O ₃	MnO
Typical agro-dark-humus podbel (fallow)								
PU	4–11	Soil	79.72 \pm 2.73	12.08 \pm 0.27	0.61 \pm 0.02	0.94 \pm 0.03	4.00 \pm 0.17	0.09 \pm 0.004
		IMN	76.56 \pm 2.30	9.29 \pm 0.20	0.35 \pm 0.01	0.78 \pm 0.03	23.81 \pm 0.88 (5.95*)	0.75 \pm 0.030 (8.33)
PU–ELnn	11–35	Soil	79.81 \pm 2.64	12.18 \pm 0.27	0.65 \pm 0.02	0.99 \pm 0.03	3.91 \pm 0.14	0.10 \pm 0.005
		IMN	76.46 \pm 2.25	8.91 \pm 0.17	0.43 \pm 0.01	0.89 \pm 0.03	23.27 \pm 0.87 (5.95)	0.66 \pm 0.026 (6.60)
ELnn	35–55	Soil	80.65 \pm 2.98	10.80 \pm 0.22	0.44 \pm 0.01	1.02 \pm 0.05	3.62 \pm 0.16	0.04 \pm 0.002
		IMN	76.82 \pm 2.36	9.79 \pm 0.21	0.41 \pm 0.01	0.97 \pm 0.03	23.46 \pm 0.90 (6.48)	0.87 \pm 0.040 (21.75)
BTnn	55–111	Soil	77.49 \pm 2.79	17.39 \pm 0.54	1.27 \pm 0.06	0.98 \pm 0.05	7.93 \pm 0.34	0.05 \pm 0.001
		IMN	76.47 \pm 2.41	11.43 \pm 0.25	0.50 \pm 0.02	0.82 \pm 0.02	17.99 \pm 0.74 (2.27)	1.63 \pm 0.049 (32.60)
BT	111–153	Soil	78.06 \pm 2.83	15.57 \pm 0.68	1.15 \pm 0.04	0.97 \pm 0.05	6.77 \pm 0.27	0.07 \pm 0.003
		IMN	77.47 \pm 2.54	11.89 \pm 0.32	0.49 \pm 0.02	0.77 \pm 0.02	11.28 \pm 0.36 (1.77)	4.27 \pm 0.155 (61.00)
C	153–192	Soil	78.10 \pm 2.65	15.70 \pm 0.61	1.15 \pm 0.04	0.99 \pm 0.04	7.04 \pm 0.32	0.13 \pm 0.006
Gleyic agro-dark-humus podbel (phytomeliorative experiment)								
PU	0–11	Soil	79.59 \pm 2.81	11.98 \pm 0.39	0.58 \pm 0.02	0.91 \pm 0.04	3.67 \pm 0.12	0.12 \pm 0.006
		IMN	77.19 \pm 2.20	9.56 \pm 0.24	0.62 \pm 0.02	0.86 \pm 0.03	16.32 \pm 0.61 (4.45)	1.99 \pm 0.047 (16.58)
PU–ELnn	11–27	Soil	79.78 \pm 2.62	12.72 \pm 0.45	0.61 \pm 0.02	0.91 \pm 0.03	3.55 \pm 0.11	0.12 \pm 0.006
		IMN	77.15 \pm 2.23	9.71 \pm 0.23	0.51 \pm 0.01	0.87 \pm 0.03	16.15 \pm 0.66 (4.55)	1.99 \pm 0.041 (16.58)
ELnn	27–49	Soil	79.96 \pm 2.78	12.40 \pm 0.48	0.66 \pm 0.02	1.01 \pm 0.05	3.90 \pm 0.13	0.22 \pm 0.011
		IMN	76.91 \pm 2.16	10.02 \pm 0.25	0.50 \pm 0.01	0.94 \pm 0.04	16.52 \pm 0.62 (4.24)	2.88 \pm 0.065 (13.09)
BTnn,g	49–83	Soil	77.78 \pm 2.70	16.63 \pm 0.74	1.31 \pm 0.05	0.92 \pm 0.03	7.30 \pm 0.29	0.18 \pm 0.006
		IMN	75.60 \pm 1.98	9.98 \pm 0.18	0.58 \pm 0.02	0.92 \pm 0.04	18.42 \pm 0.71 (2.52)	6.11 \pm 0.281 (33.94)
BTg	83–112	Soil	77.38 \pm 2.71	13.90 \pm 0.51	0.96 \pm 0.03	0.94 \pm 0.03	10.29 \pm 0.47	0.08 \pm 0.003
		IMN	76.16 \pm 2.08	9.32 \pm 0.16	0.60 \pm 0.02	0.72 \pm 0.02	21.42 \pm 0.77 (2.08)	1.76 \pm 0.039 (22.00)
Cg	112–122	Soil	78.81 \pm 2.83	15.19 \pm 0.59	1.12 \pm 0.04	0.93 \pm 0.04	10.83 \pm 0.38	0.12 \pm 0.007
Agro-dark-humus gley podbel (experiment with application of organic fertilizer)								
PU	0–27	Soil	80.14 \pm 3.17	11.55 \pm 0.34	0.44 \pm 0.01	0.99 \pm 0.04	3.60 \pm 0.13	0.05 \pm 0.002
		IMN	76.61 \pm 2.27	8.71 \pm 0.19	0.35 \pm 0.01	0.76 \pm 0.03	23.54 \pm 0.88 (6.54)	0.72 \pm 0.025 (14.40)
ELnn,g	27–42	Soil	80.86 \pm 2.99	11.95 \pm 0.37	0.57 \pm 0.02	0.94 \pm 0.03	3.82 \pm 0.14	0.04 \pm 0.001
		IMN	77.07 \pm 2.40	8.50 \pm 0.22	0.49 \pm 0.01	0.62 \pm 0.02	22.32 \pm 0.92 (5.84)	0.49 \pm 0.011 (12.25)
BTnn,g	42–91	Soil	77.59 \pm 2.73	15.65 \pm 0.62	0.93 \pm 0.04	0.99 \pm 0.04	7.43 \pm 0.30	0.03 \pm 0.001
		IMN	77.28 \pm 2.36	14.22 \pm 0.55	0.93 \pm 0.03	0.99 \pm 0.04	13.29 \pm 0.43 (1.79)	0.54 \pm 0.017 (18.00)
G	91–132	Soil	78.25 \pm 2.85	15.59 \pm 0.68	1.03 \pm 0.04	0.99 \pm 0.04	6.29 \pm 0.25	0.04 \pm 0.001
		IMN	77.41 \pm 2.64	13.98 \pm 0.55	1.10 \pm 0.04	0.97 \pm 0.04	11.23 \pm 0.45 (1.78)	0.79 \pm 0.027 (19.75)
CG	132–170	Soil	78.50 \pm 2.61	15.75 \pm 0.70	1.14 \pm 0.05	0.96 \pm 0.03	6.30 \pm 0.26	0.04 \pm 0.002

*EF, enrichment factors of elements in nodules.

and/or Mn-enriched compounds and in a lesser degree the compounds of macroelements.

Concentrations of SiO₂, Al₂O₃, MgO, and TiO₂ in IMNs of most soil horizons were lower in comparison with host soils (Table 3). The vertical distribution of macroelements in IMNs corresponded to their distribution in soil fine earth. The obtained data confirmed the assumption that the compounds of macroelements were the components of the host soil mass, which entered in IMNs in the process of their growth and development. The results of research of concentrations of macroelements in IMNs and soils agree with

regularities determined earlier for IMNs of different soil types [39, 52, 53, 58].

Concentrations of Fe₂O₃ and MnO in IMNs and soils displayed a quantitative difference among the experiment variants. Though concentrations of Fe₂O₃ in host soil were similar, maximal concentrations and accumulation were observed in IMNs of fallow soil and soil of variant with long-term application of organic fertilizer. When concentration of Fe₂O₃ in soils of these variants of the experiment increased, concentration of Fe₂O₃ in IMNs decreased. Interconnection between concentrations of MnO in IMNs and

host soil in these variants of experiment was not found. Concentrations of MnO increased in IMNs of fallow soil from the upper part of soil profile to its lower part. Maximal concentrations of MnO in IMNs of soil of variant with application of organic fertilizer were found in neoformations of upper and lower parts of soil profile. In soil of phytomeliorative variant, vertical distribution of Fe_2O_3 in host soil mass and in IMNs was similar and demonstrated the trend towards the increase of Fe_2O_3 content down the soil profile. Host soil fine earth and IMNs of this variant had higher concentrations of MnO with maximum in the middle part of soil profile.

General trend was observed for IMNs in soil towards the increase of accumulation of Fe_2O_3 in IMNs in the upper and middle parts of soil profile (horizons PU, PU–ELnn (g), and ELnn (g)) and the increase of intensity of MnO accumulation in IMNs formed in the lower part of soil profile (BT(nn,g)(g) and G horizons). Despite the higher absolute values of Fe_2O_3 content in IMNs, the intensity of MnO accumulation in nodules was higher. Maximal levels of *EF* MnO were observed in IMNs with minimal levels of *EF* Fe_2O_3 . Some antagonism in accumulation of Fe_2O_3 and MnO in IMNs was also confirmed by the distribution of elements within IMNs (Figs. 2a and 2b). Manganese concentrated mostly in the internal zone, while Fe was present in all zones of IMNs. Linear scanning of cross section of IMNs allowed revealing the peaks enriched with Fe ions in the outer zone of IMN and decrease of iron content in internal zone. Scanning of cross section of IMN reflected the alternation of stages with the increase of Fe content and those with a decrease in Mn content. The results of some authors explain the difference in element compositions of different zones of concretions and nodules by alternation of periods of soil drying and moistening and respectively by the change of redox conditions [30, 32, 56]. It was determined on the basis of these results that zones with higher Mn content were formed within concretions and nodules in dry periods, and the zones with high Fe content were formed in moist periods. However, this regularity is difficult to be used for the IMNs of studied soils, because IMNs that accumulated Mn more actively were formed in lower horizons of soil profile, which were heavy loamy and clayey, morphologically identified signs of gley (soils of phytomeliorative and with long-term application of organic fertilizer variants), and consequently longer period with reducing conditions. More active accumulation of Mn in IMNs of the lower part of soil profile was apparently connected with high mobility of Mn a wide range of Eh and capability for moving and sedimentation in microzones with local manifestation of oxidative conditions (internal zone of IMN) against the background of general of reducing conditions [30].

Varying of interaction was found on the basis of correlation analysis between concentrations and accu-

mulation of trace elements and concentrations of C_{TO} , Fe_2O_3 , and MnO in IMNs of soils in different variants of the experiment (Table 4). Chromium was an exclusion from this regularity. Concentration and accumulation of Cr in IMNs of soils of all variants had statistically significant correlation with the contents of Fe compounds in IMNs and of C_{TO} in IMNs and host soil. The values of correlation coefficients agreed with the results obtained by some authors concerning the predominating association of Cr ions with macromolecular organic ligands and with mineral colloids of Fe (hydr)oxides in different soils [22, 36, 37]. The results of the study of different compounds of Cr in soils of region of our study with similar direction of soil-forming process confirmed active participation of humus compounds with high molecular weight and polymerization degree in the distribution of water-soluble forms of Cr in soil profile [54]. Input and accumulation of Cr in IMNs of studied soils was determined by high adsorption activity of Fe-containing and organic compounds separately, as well as by the quantity of complexed Fe-organic compounds, which are present in soils and in IMNs.

Similar relationship between Fe-containing compounds and C_{TO} was found for Co concentrations in IMNs of soils of fallow and variant with long-term application of organic fertilizer (Table 4). The value of correlation coefficient between these variables decreased or had negative values in IMNs of soils of phytomeliorative variant. Despite weak correlation between the concentrations of Co and MnO in IMNs of soils of phytomeliorative variant, correlation between Mn-containing compounds of IMNs and Co accumulation was very close. In the works on specific character of selective accumulation of trace elements by the main nodule-forming components, Co is classified with elements of Mn group as well as with elements of Fe group [24, 31, 33, 42, 43, 52]. The increase of Mn content in IMNs and in host soil and, respectively, the appearance of additional reaction-active Mn-phases, which can increase Co accumulation in IMNs under the conditions of neutral and weakly alkaline reaction was the probable cause of activation of Mn-containing compounds in Co accumulation by the nodules in soils of phytomeliorative variant. The results, presented in the work [35], confirmed the increase of intensity of Co ions sorption by Mn oxides, when soil acidity decreased, and indicated high degree of Co association with anionic forms of Mn (hydr)oxides in soil Fe–Mn nodules. Concentrations of Co in IMNs of soils of fallow and variant with organic fertilizer correlated with Fe-containing compounds and with concentrations of C_{TO} in nodules and host soil. Input and transformation of Co in IMNs of soils of these variants could be determined by joint effect of the above-listed phases stimulated by some organic ligands of Co sorption by Fe-containing compounds [23].

Table 4. Pearson correlation coefficients between concentrations of C_{TO} (soils, nodules), Fe_2O_3 (nodules), MnO (nodules) and concentrations and accumulation of trace elements in nodules

Elements	C_{TO}		Fe_2O_3	MnO
	soil	IMNs		
Typical agro-dark-humus podbel (fallow) ($C_{TO} n = 24$; $MnO, Fe_2O_3 n = 30$)				
Co	+0.63*	+0.71*	+0.98*	-0.93
EF_{Co}^{**}	-0.44	-0.61	-0.37	+0.17
Ni	-0.46	-0.58	-0.92	+0.98*
EF_{Ni}	-0.49	-0.78	-0.92	+0.98*
Cu	+0.23	+0.28	+0.81*	-0.71
EF_{Cu}	+0.34	+0.40	+0.83*	-0.72
Cr	+0.48*	+0.71*	+0.62*	-0.43
EF_{Cr}	+0.64*	+0.79*	+0.77*	-0.62
Pb	-0.67	-0.58	-0.98	+0.96*
EF_{Pb}	-0.55	-0.24	-0.94	+0.98*
C_{org}	+0.85*	+1	+0.68*	-0.64
$EF_{C_{org}}$	-0.60	-0.24	+0.29	-0.13
Gleyic agro-dark-humus podbel (phytomeliorative experiment) ($C_{TO} n = 24$; $MnO, Fe_2O_3 n = 30$)				
Co	+0.26	-0.46	-0.77	+0.42*
EF_{Co}	-0.69	-0.95	+0.30	+0.96*
Ni	-0.70	-0.89	+0.43*	+0.89*
EF_{Ni}	-0.79	-0.86	+0.65*	+0.75*
Cu	+0.78*	+0.71*	-0.51	-0.38
EF_{Cu}	+0.79*	+0.75*	-0.62	-0.42
Cr	+0.41*	+0.51*	+0.68*	-0.45
EF_{Cr}	+0.72*	+0.93*	+0.37*	-0.81
Pb	-0.79	-0.78*	+0.87*	+0.81*
EF_{Pb}	+0.39	+0.10	-0.27	+0.26
C_{org}	+0.99*	+1	-0.93	-0.97
$EF_{C_{org}}$	-0.84	-0.90	+0.99*	+0.97*
Agro-dark-humus gley podbel (experiment with application of organic fertilizer) ($C_{TO} n = 18$; $MnO, Fe_2O_3 n = 24$)				
Co	+0.95*	+0.80*	+0.90*	+0.14
EF_{Co}	-0.44	+0.31	-0.28	+0.30
Ni	-0.92	-0.31	-0.96	+0.50*
EF_{Ni}	-0.71	+0.13	+0.93*	+0.77*
Cu	+0.58*	+0.43	+0.75*	-0.85
EF_{Cu}	+0.93*	+0.41	+0.97*	-0.46
Cr	+0.75*	+0.99*	+0.81*	+0.18
EF_{Cr}	+0.88*	+0.94*	+0.89*	+0.16
Pb	+0.60*	-0.22	+0.74*	-0.85
EF_{Pb}	+0.73*	-0.21	+0.72*	-0.65
C_{org}	+0.61*	+1	+0.66*	+0.95*
$EF_{C_{org}}$	-0.83	-0.05	-0.78	+0.25

*Statistically significant ($p \leq 0.05$.) Pearson correlation coefficient.** EF , enrichment factors of elements in nodules.

The level of correlation relationship in IMNs of soils of fallow and of the variant with organic fertilizer confirms referring Cu to the elements of Fe group. Application of different types of organic fertilizers was accompanied by stronger interaction between C_{TO} content and concentration and accumulation of Cu in IMNs. This regularity was substantiated by activation of complex compounds of free Cu ions with humic acids formation in the case of additional input of organic matter in soils [21, 38, 46]. Content of C_{TO} in host soil in the variant with application of organic fertilizer was characterized by very close correlation relationship with Cu accumulation in IMNs, and this allowed considering Cu-organic compounds of soil fine earth as possible sources of element incorporation to IMNs. Concentrations of C_{TO} in IMNs and in soils of phytomeliorative variant was only among considered parameters, which closely correlated with Cu concentration and accumulation in IMNs. Long-term input in soil of easily hydrolysable organic compounds is accompanied by the formation of stable as well as mobile Cu-organic complexes [54]. It is likely that mobile Cu-organic complexes are more suitable to enter IMNs. Further transformation of such compounds in IMNs is accompanied by the formation of zones of combined localization of C_{TO} and Cu within IMNs [52].

Concentrations and accumulation of Ni in IMNs correlated most closely with Mn-enriched compounds. When applied different types of organic fertilizers, the increase was observed of relationship between accumulation of Ni and Fe-containing phases of nodules. Enrichment of soils with organic matter was accompanied by the increase of Ni concentrations in soils resulting of active complex formation between Ni ions and humic acids [35]. Despite the additional input of organic matter in soils of two variants of the experiment, statistically significant positive relationship between Ni accumulation and C_{TO} content in IMNs was not found. Activation of Fe-containing phases relative to Ni in IMNs in soils of phytomeliorative variant and variant with fertilizer could be the result of the influence of additional input of organic compounds on the increase of the amount of hydrolyzed particles of Fe in soils and probably in IMNs as well [3].

The interaction between Pb and studied carrier phases significantly differed in the IMNs. Concentrations and accumulation of Pb in IMNs of soil of fallow variant was characterized by very close correlation with Mn-containing compounds. Concentration of Pb in IMNs of soils of phytomeliorative variant correlated closely with Mn- as well as with Fe-containing compounds. Concentrations and accumulation of Pb in IMNs of soil of variant with organic fertilizer statistically significantly correlated with Fe-containing compounds and C_{TO} content in soil. Obtained results confirmed the activation of the complex compounds

between Pb and high molecular organic compounds formation owing to Pb chelation by functional groups of aromatic rings, when organic fertilizer of animal origin was applied [3, 34, 48]. In general, Pb in IMNs of different soils belongs to the elements of Mn group as well as to the elements of Fe group [20, 53]. By analogy with Ni accumulation in nodules, application of different types of organic fertilizers had indirect influence on the alternation of phases participated in Pb accumulation in IMNs.

Obtained results indicated combined participation of Fe-containing and organic compounds in accumulation of trace elements by nodules. Statistically significant correlation between concentrations of Fe_2O_3 and C_{TO} was recorded in IMNs of soils of fallow and soils of the variant with organic fertilizer. This was apparently connected with longer period of organic matter transformation and formation of greater amount of stable Fe-organic compounds in soils and in IMNs of these variants of the experiment. The possibility of formation of such compounds within IMNs of arable soils was confirmed in the work [13], where the formation of microzones of C localization, on which Fe ions precipitated, was reported. Correlation coefficient between concentrations of Fe_2O_3 and C_{TO} had negative values in IMNs of soil of phytomeliorative variant of experiment, and this was caused by the difference in composition of organic residues entering the soil, processes of their transformation, and formation of the system of humus substances in soils of different variants of the experiment. Additionally, inverse interaction between these parameters could be determined by the increase of competitive effects of ions of other metals with high affinity to humic acids on Fe fixation in organic compounds. Very close correlation between Fe- and Mn-containing compounds and the value of accumulation of C_{TO} in IMNs were observed in soils of phytomeliorative variant of the experiment, and this confirmed active an participation of the main nodule-forming components in transformation of organic compounds within nodules.

CONCLUSIONS

Direct and indirect participation of humus substances in accumulation of Ni, Co, Cu, Cr, and Pb in IMNs agro-dark-humus podbels was found.

Studied IMNs are brown coarse and small nodules, and are characterized by internal differentiation by density, color, and chemical composition.

Depositing was confirmed of organic compounds in iron-manganese nodules. More active fixation of C_{TO} by nodules was observed in soils of fallow and phytomeliorative variants of the experiment, and this apparently was caused by the input of easily decomposed organic residues. The composition of humus in IMNs of such soils was characterized by domination of the fulvic acids fraction. Concentrations of fulvic acids

in nodules increased down the soil profile. The formation of highly condensed organic compounds in soils (variant with long-term application of organic fertilizer) was accompanied by the decrease of assimilation of C_{TO} by IMNs and the increase of relative fraction of humic acids. Humic acids of IMNs in soils of this variant of the experiment had lesser molecular dimensions in comparison with those in IMNs in soils of fallow and phytomeliorative variants.

The studied soils had increased concentrations of Ni, Co, Cu, Cr, and Pb in comparison with the mean values for the world soils and exceeded regional Clarke values for Cu and Cr. Active accumulation of Co and Pb was observed in nodules; Ni, Cr, and Cu accumulated in them less intensely. Greater accumulation of Pb, Ni, and Cu was observed in the fallow soil nodules, Co in nodules of soil of phytomeliorative variant, Cr in nodules of soil of variant with long-term application of organic fertilizer. The intensity of accumulation of trace elements in nodules varied in soil profiles.

General trend was observed towards the increase of Fe_2O_3 accumulation by the nodules occurring in the upper and middle parts of soil profile and the increase of MnO accumulation intensity was recorded in the nodules of lower part of the soil profile. The level of MnO accumulation in nodules was maximal among studied elements.

Variations of interactions between concentrations and accumulation of trace elements (excluding Cr) and contents of C_{TO} , Fe_2O_3 , and MnO were observed in the nodules of soils in different variants of the experiment. Concentrations and accumulation of Cr were controlled by the content of Fe compounds in IMNs and concentrations of C_{TO} in IMNs and host soil. Iron-containing compounds and C_{TO} in nodules of soils of fallow and variant of the experiment with long-term application of organic fertilizer were the factors determining Co concentrations and accumulation. The increase of MnO content in IMNs and host soil of phytomeliorative variant and the decrease of soil acidity were accompanied by activation of Mn compounds in the process of Co accumulation. Application of different organic fertilizers increased the influence of C_{TO} on concentration and accumulation of Cu in nodules, and this allowed considering Cu-organic compounds in the soil fine earth as possible sources of element entering to IMN. Along with C_{TO} , Fe-containing compounds had significant influence on Cu accumulation in IMNs in soils of fallow and variant with long-term application of organic fertilizer. In IMNs of soils of variants of the experiment, Ni was associated with the elements of Mn-group. Despite the absence of statistically significant positive correlation between Ni accumulation and C_{TO} content, activation was observed of Fe-containing phases in Ni accumulation in IMNs of soils of variants with application of different types of organic fertilizers. Concentration and accumulation of Pb were determined in the

IMNs of fallow soil by Mn compounds, while in IMNs of soil of the phytomeliorative variant by the combined influence of Mn and Fe compounds, and in IMNs of soil in the variant with long-term application of organic fertilizer by Fe-containing compounds and C_{TO} content in the soil.

Combined participation was found of Fe-containing and organic compounds in accumulation of all studied trace elements in nodules. Statistically significant correlation relationship between the concentrations of Fe_2O_3 and C_{TO} was observed in the nodules of soils with longer period of organic matter transformation and higher content of stable Fe-organic compounds (fallow and variant with long-term application of organic fertilizer).

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ETHICS APPROVAL AND CONSENT TO PARTICIPATE

This work does not contain any studies involving human and animal subjects.

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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