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BACKGROUND CONTENT OF HEAVY METALS AND ITS ENVIRONMENTAL DESCRIPTIVENESS IN SOILS OF THE UKRAINIAN POLISSYA ZONE LANDSCAPES

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The various approaches to definition of chemical elements background content have been considered. The relevant background values of heavy metals in the soil to solve the normativity agroecological challenges have been set out. This paper deals with results of a statistical analysis of the Ba, Pb, Cr, Mn, Ni, Mo, V, Cu, Zn, Sr, Co distribution throughout the zonal soil of geochemical landscapes Ukrainian Polissya . The defining factors of natural dispersion and concentration of chemical elements in the sod-podzolic and sod-podzolic gley soils have been outlined. This paper shows, by using clarks and concentration ratios, the correspondence between the characteristics of the natural migration processes with background content of heavy metals in the geochemical landscapes soil of acidic and acidic gley classes. The background content of heavy metals in the zonal landscapes of Ukraine were suggested to use in regional agroecological rationing system and selection of territories for the agricultural products cultivation.

Key words: *heavy metals, soils, background contents, Polissya , agroecological rationing.*

Introduction. The necessity to use of heavy metals background content in the soils of Ukraine as an indicator of the environment is widely covered in the normative documents and scientific researches [1-5]. To heavy metals often involves chemical elements with atomic weight of more than 50 atomic units (*amu*) and a density of 8 g/cm^3 - Zn, Co, Cu, Mo, Mn, Pb, Cr, Ni, V, Sr, Ba, and as well As, Cd, Hg.

Heavy metals background contents is a quantitative basis for soil contamination assessment and its subsequent remediation, determine associations of chemical elements of anthropogenic pollution, the estimates of the coefficients concentration ratios and total pollution index calculation to determine the degree of lands technogenic pollution and providing for technologically contaminated lands the status of polluted [3]. The system of soil properties standards indexes includes analysis of heavy metals background total forms and its comparison with clarks and maximum permissible concentrations (MPC) [2]. Survey of the fields for production of organic crops, in the soil-agrochemical monitoring of agricultural lands includes an assessment of soil pollution by heavy metals relative to the background and clark [1].

Spatial differentiation of the heavy metals background contents for soils of different landscapes is essential for direct regulation and landscapes management that declared in the European Landscape Convention [5].

Despite the importance of heavy metals background content assessments, in the practice of agro-environmental researches of Ukraine they are not used but replace the administrative established maximum permissible concentrations, or other local numbers, which are not statistically justified.

Calculated by the author the heavy metals background content in the zonal soils of Ukraine geochemical landscapes and their comparative analysis, confirm necessity of their application for an informative environmental analysis of agro-landscapes,

assessment of the anthropogenic pollution processes and self-purification of soil, selection areas for growing organic crops.

A review of the topic publications. Investigations of the heavy metals background concentrations in soils are of three main interrelated aspects - understanding the concept of "background levels", informativeness of the data source and principles of statistical calculations. In order to solve each of these questions is no unified approach.

The concept of "background content" in soils and other components of the environment has become a theoretical substantiation in the fundamental work on the geochemistry of landscapes M.A.Glazovskaya, A.I.Perel'man, N.S.Kasimov (*М.А. Глазовская, А.И. Перельмана, Н.С. Касимова)* as the distribution of chemical elements in components of landscapes, which shows the direction of their migration processes [6].

The environmental significance of the geochemical background contents for modern landscapes widely covered in the scientific works of I.A.Morozova, N.N.Moskalenko, N.G.Gulyaeva (*И.А. Морозова, Н.Н. Москаленко, Н.Г. Гуляева)* [7]. The general approach to understanding the concept of background content is natural landscape area homogeneity on terms of geochemical migration in the absence or minor technogenic impact.

For determine the heavy metals background concentrations in soils and other components of the environment there are three basic approaches: survey of sample plots outside of pollution zones, investigation of protected and recreational areas, regional landscape-geochemical analysis [2, 4, 8]. The first two approaches are in fact ignoring the natural landscape component of the assessments background content, which limits the possibility of their using on purely local level; in addition, the requirement of exceeding 20 % of the difference in humus content on the test site and site survey makes it impossible to use them in the same soil phase, taking in account that its fluctuations reach 45-85 %. An estimate of heavy metals background concentrations on the basis of the regional landscape-geochemical analysis was developed by the author over the last 10 years, also in the framework of the International *GEMAS* project [8, 9].

The principles of statistical analysis of the chemical elements distribution in the components of the environment was described O.O.Beus, A.O.Golovin, I.A.Morozova (*О.О. Беус, А.О. Головин, И.О. Морозова)* [7, 9, 10]. The formation of statistical data sample on the landscape-geochemical principles largely determines the natural-technogenic homogeneity of research objects [9-11]. On the background content of chemical elements is allowed to take as average value and the median or mode statistical sampling distribution of chemical elements in soils, waters, rocks [2, 7, 8].

The subjects of ecological and sanitary-hygienic rationing of heavy metals content in the soils of Ukraine are devoted the scientific works of V.V.Medvedev (*В.В. Медведев)* [12], T.M.Egorova (*Т.М. Єгорова)* [9] and others. The most experts acknowledge the lack of informativeness MPC of heavy metals as regional rations for ecologically safe agricultural products, justifying the complexity of solving the problem of environmental rationing of soil associating it with a variety of natural and technogenic factors of the soil layer formation. Meanwhile, until recently, for research of the complex questions of natural and technological processes differentiation in agricultural landscape of Ukraine is not given adequate attention. As a result, the background content of heavy metals in different natural soil types in terms of their agricultural use has no place in the practice of agro-ecological analysis.

The purpose of the presented researches was to assessment the heavy metals background content in the zonal soils of agricultural landscapes of Ukraine taking into account their natural basis and functional using of agricultural land.

Objects and methods of research. The presented researches are based on the materials of the regional investigation of the total forms content of chemical elements in the soil cover of Ukraine, conducted in 1989-1992, *SGE "Pivnichgeologiya*" in which the author participated [13]. Note that the total contents of trace elements in soils of Ukraine does not undergo significant changes, as evidenced by a comparison of their content in a typical soils profiles were surveyed in the 70-ies [15] and the 90-ies [16] the last century. Analytical results of spectral analysis (by the method of complete evaporation) in respect of heavy metals content in 2760 soil samples were included in the author has created a database "Ecology - 2000", which has 27 parametric and 10 nonparametric identification attributes with the identification of natural-technogenic conditions of soil formation at the observation points [8, 9].

For assess the heavy metals background concentrations in soils of Ukrainian Polissya selected local geochemical landscapes where there is no or least technogenic pressure level of technogenic changes in physical and chemical properties of the soil quality less than 30 % (recreational areas, forest land, pastures and grasslands, arable land of annual crops), homogeneous soil cover by class of geochemical migration, of plant communities, relief and overall composition of parent rocks. Such local geochemical landscapes *(LGL)* characterized 9 on the territory of the Ukrainian Polissya .

Analysis of ecological-geochemical process in Polissya landscapes was applied clarkes concentration *(C_C)* and the concentration factors *(Cf),* and the results of previous ecological-geochemical researches of the author [11, 12]. These factors are common quantitative parameters for analysis as a ratio with certain environmental standards (for example, MPC) and the direction of migration of chemical elements – concentrations (on the *Cc* and *Cf* > 1,0) and dispersion (under the *Cc* and *Cf* < 1,0) [4, 6, 8, 10].

Analysis of research results. Statistical analysis of data on regarding the distribution of heavy metals in these landscapes included the formation of normal sampling variation or lognormal law, the definition of average values *(X)* as the background levels for soils in landscape, the calculation of confidence intervals fluctuations of the background values *(t),* the coefficients of variation *(V)* and other statistical parameters for the 95% probability level (Tables 1-2).

1. Statistical estimation of heavy metals background concentrations in soils of landscape acid (H^+) and acidic calcium (H^+ - Ca^{2+}) classes migration zone of Ukrainian Polissya

Agrosoil provinces	Statistical estimations of the heavy metals contents in soils of landscapes: *X*, mg/kg (upper numeric); *t*, mg/kg (average numeric); (*V*, % (lower numeric)										
	Ba	Pb	Cr	Mn	Ni	Mo	V	Cu	Zn	Sr	Co
LGL 1 (n = 41). Soddy-podzolic soils; mixed broadleaved-pine forests; sands with interlayer's of sandy loam and loam on water-ice and glacial deposits; planar and undulating moraine outwash plains (H^+).											
The Right-Bank Polissya	142,2	8,7	14,1	393,0	4,3	0,7	9,3	29,9	30,8	59,0	1,7
	31,7	1,2	3,8	117,1	0,6	0,1	3,2	10,6	4,7	6,1	0,4
	63,0	36,3	68,2	58,6	37,7	43,0	84,2	48,4	38,5	29,9	64,8
LGL 2 (n=27). Soddy-podzolic soils; willows with grasses and cereals meadows, aspen, reed, alder, hipnum; drained biogenic and lake- biogenic peat formations; flat slightly wavy floodplain lowland rivers (H^+).											
The Right-Bank Polissya	128,5	11,2	15,7	413,3	4,7	0,7	10,0	47,1	49,4	58,9	2,2
	44,5	3,6	7,5	115,5	1,5	0,1	2,3	30,2	23,5	6,8	0,6
	76,6	69,3	86,9	74,1	72,3	43,0	45,4	58,1	47,2	27,8	71,3

LGL 3 (n=15). Soddy-podzolic soils; arable lands in the places of coniferous and deciduous forests; loess and loess loam; slightly tilted flat alluvial plain of the first and second above the floodplain of river and lake terraces (H^+).											
The left-Bank Polissya high	190,0	20,5	29,5	576,2	9,1	0,5	17,8	35,5	65,1	1,9	3,8
	53,9	6,8	7,4	228,1	2,7	0,1	3,7	12,2	14,6	29,8	1,1
	50,7	66,0	49,5	66,1	52,4	29,5	34,6	45,4	44,4	66,5	56,6
LGL 4 (n = 19). Meadow and chernozem-meadow soils; willows with grasses and cereals meadows; sandy alluvial deposits; flat slightly wavy floodplain lowland rivers (H^+ - Ca^{2+}).											
The left-Bank Polissya high	181,2	13,5	29,6	444,2	13,1	1,0	26,1	28,8	60,0	104,9	4,9
	65,3	3,8	12,0	119,0	5,7	0,2	7,5	8,6	20,0	31,0	1,2
	66,0	62,4	90,5	59,6	97,5	55,7	63,9	45,8	74,3	65,7	52,5

2. Statistical estimation of heavy metals background concentrations in soils of landscape acid gley class migration zone of Ukrainian Polissya

Agrosoil provinces	Statistical estimations of the heavy metals contents in soils of landscapes: *X*, mg/kg (upper numeric); *t*, mg/kg (average numeric); (*V*, % (lower numeric)										
	Ba	Pb	Cr	Mn	Ni	Mo	V	Cu	Zn	Sr	Co
LGL 5 (n=18). Soddy-podzolic gley soils; mixed broad-leaved pine and pine forests, often arable after the forest meadows; biogenic and lake-biogenic peat formation, alluvial sands; planar and undulating moraine outwash plains.											
The Western Polissya	120,0	14,3	21,5	482,2	5,2	0,9	14,8	30,4	40,9	64,3	2,2
	28,1	15,4	7,7	162,0	2,7	0,2	3,8	11,9	27,1	19,7	0,6
	45,8	14,2	77,6	72,7	85,2	34,6	55,0	48,5	37,4	58,0	43,8
LGL 6 (n=19). Soddy-podzol gley soils; arable land on the site of coniferous and deciduous forests; fluvioglacial, ice and ancient ice deposits; planar and undulating moraine outwash plains.											
The Right-Bank Polissya	227,9	18,5	38,1	643,2	14,2	1,1	33,6	25,0	52,4	76,9	6,0
	57,4	15,8	12,3	174,1	5,5	0,2	12,5	6,1	13,9	12,6	2,5
	56,0	19,0	71,7	60,2	86,4	40,0	82,8	40,0	45,6	36,5	91,3
LGL 7 (n=13). Bog and peat soils; arable land on the site of coniferous and deciduous forests; sands with interlayer's of sandy loam and loam on fluvioglacial, ice and ancient glacial deposits; not drained relating to basin-hollows areas of floodplains, river terraces and outwash plains.											
The Western Polissya	293,1	29,7	38,4	538,7	19,0	1,0	39,5	42,3	98,2	99,6	6,7
	92,0	18,0	25,8	144,1	6,8	0,2	14,3	19,8	35,6	39,5	2,4
	57,8	48,8	70,8	49,2	65,9	38,9	66,4	52,3	66,7	47,0	65,0
LGL 8 (n=41). Bog and peat soils; arable land on the place of the dried herb bogs and boggy meadows; sands with interlayer's of sandy loam and loam on fluvioglacial, ice and ancient glacial deposits; flat undulating lowland floodplain rivers.											
The Western Polissya	226,8	14,4	36,1	399,3	11,1	0,7	24,7	35,4	57,1	82,6	4,1
	39,1	3,2	8,4	97,1	2,6	0,1	6,2	10,3	39,1	3,2	8,4
	56,3	39,2	75,8	63,0	77,5	37,3	82,0	43,4	56,3	39,2	75,8
LGL 9 (n=18). Soddy gley soils; arable land on the site of coniferous and broadleaves forests; sands with interlayer's of sandy loam and loam on fluvioglacial, ice and ancient glacial deposits; planar and undulating moraine outwash plains.											
The left-Bank Polissya high	143,4	16,1	25,0	886,7	5,9	0,7	11,6	26,8	51,8	84,7	3,4
	51,5	9,6	8,7	216,5	1,7	0,2	6,1	13,5	22,2	36,2	1,3
	66,7	92,5	74,9	52,8	46,1	61,2	67,0	49,7	47,9	75,3	81,0

Obtained the quantitative data testify to certain fluctuations of the heavy metals background concentrations in soddy-podzolic and soddy-podzolic gley soils landscapes of Ukrainian Polissya . Environmental information of heavy metals background concentrations obtained values are estimated on the ecological-geochemical factors that allow installing the peculiarities of landscape heavy metal migration processes – clarkes concentration *(C_C)* and the concentration factors *(Cf).*

Taken into account the dynamic nature of distribution and balance of chemical elements in geochemical landscape and geochemical processes of migration and environmental compliance ranked in three categories: state of equilibrium and environmental compliance background concentrations of heavy metals on the condition of the values of *Cc* and *Cf* from 0,5 to 1,5; intensive dispersion – if *Cc* and *Cf* values are less than 0.5; intense concentration – if *Cc* and *Cf* are of than 1.5. Clarkes concentration calculated for world clarkes content of chemical elements in soils by *N. Bowen* (1979) and clarkes their concentration in soils of Europe [14]; the concentration ratios - up to MPC [1] and statistical evaluation of the regional background for arable lands of Ukraine

[8], which were obtained by semi-quantitative spectral and X-ray fluorescence analysis in the framework of the international project on geochemical mapping of Europe agricultural lands in 2009-2011 (Tables 3-4).

3. The clarkes concentrations of heavy metals background content in soils of the Ukrainian Polissya zone landscapes (relatively to soil clarkes)

Classes of geochemical landscapes	Clarkes of heavy metals background concentrations in soils of landscapes relatively to clarkes in soils of the World (above the line) and Europe (below the line)										
	Ba	Pb	Cr	Mn	Ni	Mo	V	Cu	Zn	Sr	Co
Sour and acidic calcium (H^+, H^+ - Ca^{2+})	0,3-0,4 0,3-0,5	0,7-1,7 0,4-1,0	0,2-0,4 0,2-0,5	0,4-0,6 0,7-1,0	0,1-0,3 0,2-0,7	0,4-0,8 0,5-1,0	0,1-0,3 0,1-0,4	0,1-1,6 2,1-3,5	0,3-0,7 0,5-1,0	0,01-0,4 0,02-1,1	0,2-0,6 0,2-0,6
Sour gley (H^+ - Fe^{2+})	0,2-0,6 0,3-0,8	1,2-2,5 0,7-1,4	0,3-0,5 0,3-0,6	0,4-0,9 0,7-1,5	0,1-0,4 0,3-0,9	0,5-0,9 0,7-1,1	0,1-0,4 0,2-0,6	0,8-1,4 1,8-3,1	0,5-1,1 0,7-1,6	0,3-0,4 0,7-1,0	0,3-0,8 0,3-0,9
Clark in soils of the World, mg/kg [14]	500	12	70	1000	50	1,2	90	30	90	250	8
Clark in soils of Europe, mg/kg [8]	375	21,5	63,5	597	20	1	70	13,5	62	97	7,6

4. The concentrations coefficients of heavy metals background content in soils of Ukrainian Polissya landscapes (relatively to the MPC and regional assessments)

Classes of geochemical landscapes	The concentrations coefficients of heavy metals background content in soils of landscapes relatively MPC (above the line) and arable land in Ukraine (below the line)									
	Ba	Pb	Cr	Mn	Ni	Mo	V	Cu	Zn	Sr
Sour and acidic calcium (H^+, H^+ - Ca^{2+})	nd 0,3-0,5	0,4-1,0 0,5-1,2	0,1-0,3 0,2-0,4	0,3-0,4 0,6-0,9	0,2-0,5 0,2-0,5	nd 0,3-0,6	0,1-0,2 0,1-0,4	nd 2,0-3,2	0,4-0,8 0,6-1,3	nd 0,02-1,1
Sour gley (H^+ - Fe^{2+})	nd 0,3-0,8	0,7-1,5 0,8-1,7	0,2-0,4 0,3-0,5	0,3-0,6 0,6-1,6	0,2-0,8 0,2-0,7	nd 0,4-0,7	0,1-0,3 0,2-0,6	nd. 1,7-2,9	0,5-1,2 0,8-1,9	nd 0,7-1,0
MPC in soil, mg/kg [1]	nd	20	100	1500	25	nd.	150	nd.	85	nd
The average content in soils of arable land in Ukraine, mg/kg [8]	376	17,3	74,7	628,3	26,1	1,6	68,8	14,5	50,7	98,1
Note: nd - no data										

Migration (concentration and dispersion) of chemical elements in the Polissya landscapes is mostly of water-salt nature, characteristics of which determines the intensive spreading of the majority of chemical elements, including heavy metals, poor concentration of nutrients by fulvic acids humus of soils, distribution of fresh hydrocarbonate calcium surface waters with a pH of 5 to 7.5 which enriched with organic substances. The predominance in the soil absorbing complex easily movable fulvic acids, as well as regional soil-forming podzolization processes, promote the intensive removal and export from the soil profile of many essential elements (Fe, Mn, Sr, Ba, Zn, Cu, V, Mo, Co, and others). Common feature of soils and parent rocks is the leaching of elements mobile forms and, consequently, the formation of low-contrast lithogeochemical anomalies of natural origin genesis and technogenic zones of pollution by heavy metals. Spatial peculiarities of natural and natural-technogenic heavy metals migration on the territory of the Ukrainian Polissya caused of sour (H^+), sour gley (H^+-Fe^{2+}) and acidic calcium (H^+-Ca^{2+}) classes of geochemical landscapes.

According to classifying of A.I.Perel'man (*А.И. Перельман),* sour class of landscapes due to the spread of varieties of soddy-podzolic soils and are characterized by high mobility and dispersion (removal) of all chemical elements; landscapes of

acidic gley class - spread of soddy-podzolic and soddy gleyed and wetland soils types, and are characterized by a decrease in mobility of oxygen- gley physical-chemical barrier of Cu, Mo, V, Cr, Mn [6, 10, 11].

Calculated clarkes values concentration of soil Ukrainian Polissye landscapes indicate the progress of natural processes of heavy metals dispersion by the assessments of heavy metals background content for soil of Ukrainian Polissya landscapes (Table 3). Distribution the physical and chemical barriers of sour gley landscapes manifest with systemic increase *Cc* in soils of these landscapes, indicating a low heavy metals concentration as associations of oxygen-gley barriers (especially, Mn and Cr), and the sorption (especially Zn and Sr) barriers.

Compliance the background assessments (Cc = 0,5-1,5) of soils clarkes in Europe are spread much more than the clarkes in World and are, respectively, 50 % and 29 % for soils of sour landscapes classes and 69 % and 49 % for soils of sour gley landscapes classes. The intensive dissipation (Cc < 0,5) recorded less widely when comparing the background assessments with clarkes in Europe, than the clarkes in World and represent 41 % of the Cc of soil sour landscapes classes, and 20 % sour gley. A significant excesses of the Cu content in soils of Ukrainian Polissya than clark in Europe (Cc = 1,8-3,5) and the average estimates for arable lands of Ukraine (Cc = 1,7-3,2), given the low values of this element mobile forms according to preliminary investigations, requires, in our opinion, for additional analytical refinements of mentioned regional assessments.

These patterns of natural processes in the soil Ukrainian Polissya landscapes are fully correspond to the levels of *Cf* (Table 4). 96 % of calculated background values of heavy metals below the exposure MPC limits and only 4 % do not significantly exceed them (*Cf* = 1,2-1,5). This ratio is saved and compared background values with the average estimates of heavy metals (except Cu) in the soils of arable lands of Ukraine: 93 % of the background values lower than the average over arable land and only 7 % higher (*Cf* = 1,1-1,9). It is saved the correlation between the background values by class of landscapes: their correspondence with average marks for soils of Ukraine arable lands (*Cf* = 0,5-1,5) describes 70 % of the value of landscapes sour gley class and 50 % - sour classes.

Conclusions. The natural peculiarities of heavy metals content and processes of their migration in soils of the Ukrainian Polissya reflect calculated by the author the background values of Ba, Pb, Cr, Mn, Ni, Mo, V, Cu, Zn, Sr, Co contents for zonal geochemical landscapes with specific soil and vegetation, geo-morphological and functional characteristics. The calculations of ecological-geochemical factors and their analysis showed consistency background values with the main natural processes of heavy metals scattering of in landscapes sour and sour gley class for minor concentrations at the landscape barriers oxygen- gley and sorption types. This confirms the representativeness of the chosen landscapes and the obtained estimates of the heavy metals concentration as a natural background for zonal landscapes of Ukrainian Polissya. The practical application of the obtained results is the introduction background concentrations of heavy metals for calculations of total pollution, agrochemical control and monitoring of soils. Research results should initiate a regional system of environmental regulation the state of agro-landscapes and remediation status agrolandscapes areas. The introduction of landscape-geochemical parameterization on agro-ecological criteria will allow to raise the importance of the agrochemical selection areas scientific basis for growing organic products on the territory of Ukraine.

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