ENVIRONMENTAL ASSESSMENT OF HEAVY METALS CONTENT IN SOIL-PLANT SYSTEM

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Abstract. The content of heavy metals (Ag, Cd, Sn, Cs, Ba, La, Rb, Sr, Mn, Fe, Cu, Zn) has been determinate in the soil-plant system: cambic chernozem - winter wheat. It was found that the amount of Ag, Sb, Sn and Ba are accumulating in soil, exceeds the admissible concentration limit. In winter wheat, the content of Cd, Fe and Zn exceed the maximum admissible concentrations. The Rb, Mn, Zn accumulates in the winter wheat grains, and Fe and Cu – in the vegetal organs of wheat.

Keywords: cambic chernozem, winter wheat, heavy metals, concentration, environmental pollution.

Introduction

Heavy metals are considered hazardous environmental pollutants. Their high concentration in plants causes inactivity of enzymes, disturbing processes of photosynthesis, respiration, transpiration, water regime, and absorption, nutrients movement in plants. Accumulation in great amounts in plants and penetrating trophic cycles, heavy metals causing various toxic diseases in human and animal organisms.

The main local sources of environmental pollution with heavy metals are industrial and municipal wastes, gas and smoke exhaust of the electric power station, uncontrolled application of fertilizers and pesticides [1]. A significant source of environmental pollution has transport that gives annually about 500 tons of harmful substances, including some heavy metals. Exhaust emissions in rural areas consist 36%, in urban area – 80%. The exhaust gases contain Pb, which share the environment pollution can be up to two thirds. In processes of tire vulcanization is used Zn and Cd, the grinding or burning these conducts to dispersed elements in the environment. As a result of research on the content of heavy metals (Pb, Cd, Zn, Cu, Mn) in soils was found a high concentration in the vicinity along roads and auto streets, on both sides [2]. In many cases the concentration of heavy metals in soils exceeds the maximum permissible concentration (MPC) in three times. Plants around of the auto roads are also polluted with heavy metals [3].

In addition to local pollutants, the Republic of Moldova is affected by smoke gas flow entering with air masses from neighboring countries, brought by winds. This impact becomes more intense: in the 80s the acid rains consisted 1/3 from total amount of rain fall, in the present – about 70% [4,5]. The accumulation of heavy metals in plants from smoke and exhaust gas takes place both by root uptake from soil and foliar from air.

According to the research, most soils of republic are weakly and moderate polluted with heavy metals [6]. To soil pollution with heavy metals contribute the exaggerate administration of fertilizes, which are contained in the composition chemical elements as ballast or added specially (superphosphate ennobled with zinc), soil fertilization with wastes, application of pesticides. Calculations show that mineral fertilizers administrated in the soil in dose of $(NPK)_{100}$, contain in g/ha: Pb-10, Ni-2, Zn-50, Cu-36, Cr-59, Cd -2 [7]. During three decades the carbonate chernozem was fertilized annually with high doses of fertilizers, the total quantity of Zn was 143 mg/kg [8]. Some guidelines show the MPC of Zn in soils – 100 mg/kg [9].

Material and method

Research has been conducted at the Experimental station "Ivancea" of Institute of Pedology, Agrochemistry and Soil Protection "Nicolae Dimo" on the Cambic chernozem. As organic fertilizer was used sludge from wastewater treatment. Were determinate heavy metals content in soil and plants which are studied and insufucient studied in Moldova. The total content of elements (Ag, Cd, Sn, Cs, Ba, La, Rb, Sr, Mn, Fe, Cu, Zn, Br) in soils and plants was determinate in Laboratory of Nuclear Reactions "Gh. N. Flerov", Institute for Nuclear Research Unit (Dubna), X-ray spectrometric method of determination, Camberra 1000.

Results and discussion

1. Heavy metals in soils

Silver (Ag) clark in lithosphere is 0,7 mg/kg, in pedosphere - 0,1 mg/kg [10, 11]. The average content of Ag in the parental rocks is 0,35 mg/kg, in soils – 0,5 mg/kg. Optimal amount of Ag varies from 0,1 to 1,8 mg/kg [12]. The technophility (ratio of element mass produced to his clark content) of Ag is $>10^{10}$ [13]. According to the results amount of Ag in soils of Moldova varies from 0,4 to 2,0 mg\kg, the avarage content is 1,2 mg\kg [14, 15]. Clear regularity in

the distribution of Ag in soil profile is not observed. According to gradation the quantity of Ag in soil can be assessed as medium and high, MPC of Ag is 1 mg\kg [16]. From this criteria, should be mentioned that in most soils of Moldova the Ag concentration is higher than MPC. In the arable layer of cambic chernozem Ag content varies within 1,0-1,3 mg/kg and is evaluated as high (table 1).

Table 1

Heavy metals in Cambic Chernozem clay-loamy, mg/kg

Variant and depth, cm		Ag	Cs	Ba	La	Ce	Nd
Control,	0-20	1,3±0,1	11±2	510±30	50±5	110±20	40±5
$N_{120}P_{4,5}K_{60}$,	0-20	1,0±0,1	12±1	490±30	50±5	120±20	40±5
Sludge, 80 t/ha,	0-20	1,3 ±0,1	13±2	480±30	40±5	110±20	40±5
Sludge, 80 t/ha,	20-40	1,3±0,1	18±2	500±30	50±5	110±20	40±5

Cadmium (Cd) – pollutant, which refers to substances excessively dangerous, I class [17]. Clark's in the litoshre is 0,13 mg Cd/kg, in pedosphere – 0,5 mg/kg [10, 11]. The average content of Cd varies from 0,1-0,6 mg/kg in parental rocks, to 0,2-0,84 mg/kg in soils, averaging 0,4 mg\kg [24]. According to the previously results obtained by the spectrographic metod Cd content in soils varies in limits 1,2-1,5 mg/kg [8].

The soil samples analyzed in the years 1960- 1965, a period without intensive application of chemical fertilizers and possible pollution of soils, the average amount of Cd was 0,41 mg/kg, the limit of variation 0,18-0,84 mg/kg [18]. The other sources mentioned that the amount of Cd in soils varies within 0,2-1,2 mg\kg [19]. Other authors marked concentrations within 0,76-1,76 mg/kg [20]. Technophility of Cd is 10^8 [13]. Annualy with fertilizers are incorporate in soil 3-4 g Cd/ha [21,22]. In the arable horizons of fertilizers soil the amount of Cd exeected MPC - 2 mg\kg. In the analyzed soil samples of cambic chernozem the amount of Cd consists 1,2-3,1 mg/kg, the average 1,9 mg/kg [14,15].

Stanium (Sn), the clark in lithosphere is 2,5 mg/kg, in pedosphere – 10 mg/kg [10, 11]. The content of Sn in rocks varies in limits 1-10 mg\kg, average 5,4 mg\kg [12]. Technophility - Sn $>10^8$ [13]. MPC of Sn is 4,5 mg/kg, according to gradation, Sn amount is higher - 8-15 mg/kg [16]. MPC value of Sn 4,5 mg/kg in 2,5 times lower than the pedosphere (10 mg/kg), which considerd the restriction underestimated. In this case is proposed a concentration 20 mg/kg of Sn in soils [16]. In the arabile cambic chernoziom Sn content consists 13 mg/kg and be considered high for soils of Moldova.

Stibium (Sb) as a polluting substance refers to II class moderately hazardous [17]. Clark Sb in litisphere consists - 0,5 mg/kg, in pedosphere – 1,0 mg/kg [10, 11]. The average content of Sb in parental rocks is 0,5-3,0 mg/kg, in soils – 1-5 mg/kg, averaging 2,0 mg/kg [12]. Technophility Sb $>10^8$ [13]. According to results the investigated soil contain Sb in limits 4,3-9,0 mg/kg, averaging 6,6 mg/kg [14, 15]. In conformity with gradation 4,1 mg/kg this content in soil is considered very high – MPC of Sb in soil is 4,5 mg/kg, for soils of Moldova is proposed 5,0 mg/kg [16]. Mention that Sb concentration in soil samples exceeded the MPC and incadred within the low polluted degree. Arable soil layer contains 7 mg/kg Sb and is considered to be weakly polluted.

Cesium (Cs) in the lithosphere is 3,7 mg/kg, in pedosphere - 5 mg/kg [10, 11]. The content of this element in rocks and soils of Moldova varies in limits 1-14 mg/kg, averaging – 5 mg/kg [12]. Technophility Cs $>10^6$ [13]. The results show that the content of Cs in soils varies within 8-21 mg/kg, averaging 14,1 mg/kg [14, 15]. Increasing the Cs content was detected in fertilized soils with sludge in dose 80 t/ha. In this variant was found a tendency to increase the amount of Mn (1300-1590 mg/kg), Cr (100-151 mg/kg), Cu (28-34 mg/kg [8, 22]. The urbam sludge contain Mn - 160-870 mg/kg, averaging - 300 mg/kg; Cr - 70-830 mg/kg, averaging -364 mg/kg; Cu – 59-1347 mg/kg, averaging - 486 mg/kg [12]. The fertilizer increased the content of elements in soil.

Bariun (Ba) – refers to substances polluting excessively dangerous I class. Clark's in the lithosphere is 650 mg/kg, in pedosphere - 500 mg/kg [10, 11]. Ba content in rocks is 60-490 mg/kg, averaging - 360 mg/kg; in soils - 140-640 mg/kg, averaging - 460 mg/kg [12]. According to results the Ba content in soils varies within 310-540 mg/kg, averaging 452 mg/kg [14,15]. The MPC of Ba in soils is relatively small - 100 mg/kg, in this context is proposed for soil of Moldova – 1200 mg/kg [12]. In the experimental samples of cambic chernozem is founded 480-510 mg/kg, being in the moderate class of toxicity.

Strontiun (Sr) – referes to substances polluting excessively dangerous, I class. Clark Sr in the lithosphere is 340 mg/kg, in pedosphere – 300 mg/kg [10, 11]. Sr content in rocks varies within 40-800 mg/kg, averaging – 210 mg/kg, in soils – 50-400 mg/kg, averaging – 240 mg/kg [12]. MPC of Sr in soils consists – 600 mg/kg [16]. In the cambic chernoziom Sr consists in arable stratum 99 mg\kg and considered very low [8, 16].

Manganese (Mn) concerns as substances polluting excessively dangerous I class. Clark Mn in lithosphere is 1000 mg/kg, in pedosphere – 850 mg/kg [10,11]. Mn content in the rocks is 180-900 mg/kg, averaging 610 mg/kg, in soils – 150-2250 mg/kg, averaging 790 mg/kg [12]. MPC of Mn in sois is 1500 mg/kg [16]. In arable horizon of cambic chernoziom Mn content is 1320 mg/kg and considered highly toxic.

Copper (Cu) as a moderate pollutant refers to substances hazardous of II class. Clark's in the lithosphere is 47 mg/kg, in pedosphere – 20 mg/kg [10,11]. The Cu content in rocks varies within 2-34 mg/kg, averaging 22 mg/kg, in soils 2-400 mg\kg, averaging - 32 mg/kg [12]. In the arable horizon of cambic chernoziom content of Cu is 28 mg/kg, considerate moderately toxic. MPC of Cu in soils is 60 mg/kg, but it is proposed for soils of Moldovs – 150 mg/kg [16].

Zinc (Zn) as a pollutant refers to excessively dangerous substances, I class. Clark in the lithosphere is 83 mg Zn/kg, in pedosphere – 50 mg Zn/kg [10,11]. Zn content in the rocks varies within 5-162 mg/kg, averaging 65 mg/kg, in the soils - 10-166 mg/kg, avaraging 71 mg/kg [12]. In the arable layer of cambic chernozem Zn amount is 39 mg/kg is considered low. MPC of Zn in soil consist 300 mg/kg, it is proposed - 250 mg/kg [16].

Lanthanum (La) clark in pedosphere is 40 mg/kg [10,11]. The amount of La in soils varies within 30-60 mg/kg, averaging 44 mg/kg [14,15]. The experimental soil contains the 40-50 mg La /kg (tab.1).

Cerium (Ce) clark in pedpsphere is 50 mg/kg [10,11]. The concentration in soils varies in limits 70-130 mg/kg, averaging 99 mg/kg. The experimental soil samples contain Ce within 110-120 mg/kg.

Neodium (Nd) content in soils varies within 30-50 mg/kg, averaging - 35 mg/kg [14,15]. In the experimental soil is founded 40-50 mg Nd/kg.

2. Heavy metals in plants

Silver (Ag) content in cereal grains varies within 0,01-0,1 mg/kg, in vegetal organs of wheat - 0,05-0,2 mg/kg [12]. According to researches, the amount of Ag in grains of winter wheat is 0,044 mg/kg, in vegetal organs – 0,026-0,035 mg/kg. The content of Ag in cereal grains in condition of Moldova less than 0,01 mg/kg is considered deficient, more than 1,0 mg/kg considered excess toxical [12]. So, the amount of Ag in winter wheat in the ecological aspects is considerate as optimal (tab.2).

Table 2

Heavy metals in winter wheat, mg/kg of dry mass

Variant	*Organ*	*Ag*	*Ba*	*Rb*	*Sr*	*Mn*	*Fe*	*Cu*	*Zn*	*Br*
Control	Grain	0,044	12	8,0	5,15	11,7	150	9	70	15,0
	Chaff	0,044	5	6,0	4,45	12,4	130	5	70	2,1
	Straw	0,044	8	5,6	11,68	20,1	130	5	70	3,5
$N_{120}P_{4,5}K_{60}$	Grain	0,044	12	8,0	6,43	11,7	140	9	70	15,0
	Chaff	0,032	7	3,0	3,03	14,9	140	5	70	6,0
	Straw	0,026	21	3,8	8,03	40,0	210	5	70	13,0
Sludge, 80 t\ha	Grain	0,044	11	3,4	7,10	85,0	280	8	66	15,0
	Chaff	0,035	7	5,6	2,83	34,5	160	5	66	9,0
	Straw	0,035	9	2,7	13,7	81,0	81	6	66	9,0

Cadmium (Cd) content in cereal grains varies in limits 0,01-0,5 mg / kg, in vegetative organs - 0,01-0,8 mg / kg [12]. According investigation, in the variant with sludge application, 80 t/ha the quantity of Cd in grains is 0,9 mg/kg, in vegetative organs – 0,2-0,3 mg / kg. In condition of Moldova the quantity of Cd in winter wheat is consider weakly toxic, and >12 mg / kg – excessive toxic. Maximum allowable level of Cd in grains is 0,3 mg/kg, in bakery products – 0,02 mg/kg [12].

Stanium (St) content in winter wheat chaff and straw varies in limits 0,05-0,14 mg/kg.

Cesium (Cs) content in wheat grains is 0,19 mg/kg, in leaves - <0,1 mg/kg, in straws - 0,14 mg/kg.

Barium (Ba) content in wheat grains is 1-10 mg/kg, in chaff and straw – 10-50 mg/kg [12]. According to researches the amount of Ba in wheat grains is 11-12 mg/kg, chaff – 5-7 mg/kg, straw – 8-22 mg/kg, leaves – 18-20 mg/kg. Ba amount in grains exceeds the normal content. In condition of Moldova Ba content in cereal grains <1 mg/kg considered weakly dangerous and >200 – surplus of content [12].

Lanthanum (La) content in wheat grains is 0,6 mg/kg, in leaves - 0,4 mg/kg, in the stems - 0,6 mg/kg. As mentioned above, the amount of this element in soil and plants is studied insufficiently.

Rubidium (Rb) content in cereal grains varies within 1-5 mg/kg [12]. In wheat grains investigated Rb amount varies in limits 3,4-9,9 mg/kg, chaff – 3-6 mg/kg, leaves – 4,0-4,8 mg/kg, strain - 2,7-5,6 mg/kg. The small amount of Rb was detected in grains on variant with sludge application.

Strontium (Sr) content in cereal grains is 1-15 mg/kg, in vegetal organs – 30-140 mg/kg [12]. According investigations the quantity of Sr in winter wheat grains consists – 15,5 mg/kg, pulp - 13 mg/kg, in chaff - 2,83-4,45 mg/kg, leaves - 17,6-25,6 mg/kg, stems - 8,03-13,7 mg/kg. The quantity of Sr in wheat grains <10 considered poor and >200 – toxical [12].

Conclusion

The concentration of Ag, Sb, Sn, Ba in the soil exceeds the MPC. High content of Cd in the arable layer of

cambic chernoziom can be explained by intensive management of mineral fertilizers containing Cd as ballast. In the variant with sludge (80 t\ha) the content of Cs increased from 11 to 18 mg/kg, Mn - 1230 - 1590 mg/kg, Cr - 100 - 151 mg/kg, Cu - 28 - 34 mg/kg. The quantity of Cd, Fe, Zn, Ba in wheat grains exceeds MAC. In grains accumulation of Br, Rb, Mn, Zn, Fe, Cu is optimal.

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