MONITORING OF CONTAMINATION OF THE ENVIRONMENT IN BUKOVYNA WITH HEAVY METALS

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Abstract. *The main sources of soils contamination with heavy metals have been analyzed. The results of monitoring agricultural soils contamination with heavy metals and the content of metals in the plant tissues in Chernivtsi region have also been registered.*

The average content of heavy metals in the agricultural soils of Chernivtsi region complies with the corresponding background values. An average content of the following heavy metals in a 0-5 cm horizon of the agricultural soils of Chernivtsi region was registered (mg/kg): 9,6 (Pb), 0,26 (Cd), 30,4 (Cu), 30,5 (Ni); 72,0 (Cr); 78,3 (Zn); 973 (Mn). Similar values for the urban soils within Chernivtsi were noticed as well: 51,3 (Pb), 0,3 (Cd), 79,2 (Cu), 25,3 (Ni); 41,0 (Cr); 73,4 (Zn); 654 (Mn).

Heavy metals were arranged in a sequence according to their toxicity, which also varies for different organisms and content of free ions. The dependence of the metal ions content in food and the plants growing and cooking conditions has been analyzed. Some ways of heavy metals accumulation in plants are described.

Local areas with higher concentration of heavy metals have been identified near roads and within some gardens. No such areas were found near industrial objects. The content of heavy metals in the soils of Prykarpattya and Prut-Dnister upland area remains below the background level, which ensures secure conditions for agricultural activities.

A comparison between the heavy metals content in Bukovyna and other regions of Ukraine has also been made.

Keywords: *monitoring of soils, accumulation of heavy metals, plants, human body, food chain.*

Contamination of the environment with heavy metals compounds is very dangerous since they can get into the human trophic sequence. The more stages consists the sequence, the higher accumulation ratio of toxic agents can be reached at the end. It is known that every new stage of the sequence results in about ten times higher concentration of the toxic agents.

Investigation of the environmental contamination with heavy metals is quite a topical issue, which includes the study of pollutants toxic action on organisms, possible accommodation of the organisms for functioning in a polluted environment, the study of various controllable and uncontrollable parameters' effect on the transformation of pollutants. In this way we can simulate and forecast possible results of eco-catastrophes and massive pollution of the environment and promote better natural self cleaning by using plants, which can absorb pollution agents.

Chemical compounds of heavy metals cause structural changes in the soils microcenosis. Sensitive species are being gradually substituted by more metal-resistant ones and rehabilitation of the metal-polluted soils requires fixation of heavy metals compounds in the indelible organomineral complexes.

Heavy metals can be allocated in the following descending toxicity sequence: mercury; silver; copper; cadmium; zinc; lead; chromium; nickel; cobalt. However, this sequence can be rearranged for different organisms and depending on the nature of the acting compounds (free ions, inorganic or organic compounds) [1].

Heavy metals ions oppress the functions of organisms by the ferment systems blocking, strong bonding with the sulfide groups and the cell walls crippling [1].

Some microbes normally require ions of cobalt, copper, iron and others, which can be part of bioactive compounds: ferments, vitamins and pigments. These ions are important agents, which ensure normal redox processes, which occur in a cell. Some ions are necessary to ensure normal structure and functioning of the microbial ribosome.

Micromycets, yeasts, some thionic microbes and pathogenic microorganisms are the most metal-resistant. This resistance can be caused by their ability to accumulate and fix the heavy metal ions in the cells. Therefore, the intracellular content of heavy metals can become hundreds times higher comparing with the corresponding concentration in the environment. Mycobacteria and actinomycetes are less metal-resistant.

Therefore, it is important to know the possible ways how heavy metals ingress in the human and animal trophic sequence and their concentrations in the soils and environment. In this way we can effectively counteract the metals accumulation. We briefly describe some of these ways below.

Some compounds of lead were used to prevent detonation in the internal combustion engines for a long time. Tetraethyl lead (TEL) was the most widely used detonation preventer. The fine dust of lead is formed as a result of TEL decomposition inside the engine and then this dust is being released together with other combustion products. Long exploitation of TEL resulted in significant accumulation of various lead compounds along many roads. Car-related emission of lead made about 80 % of the total anthropogenic lead emission. Hard cars traffic also results in emission of some other toxic agents: compounds of cadmium, zinc, copper, oxides of nitrogen, carbon (II), hydrocarbons and aldehydes.

Cadmium can be emitted as a result of car tires wearing, destruction of asphalt road cover, leakage of engine oils and, slightly, from the old and worn-out cadmium-nickel batteries with destroyed bodies.

Many compounds of manganese are used in engineering and medicine. The manganese (IV) oxide can be used as doping for some special steels, for discoloration of the glass mass, for production of linoleum, some dyes and lacquers. Potassium permanganate can be used in medicine as a disinfectant [2].

Ferrous and nonferrous metallurgy, thermoelectric power plants, mineral fertilizers and pesticides production, irrigation and melioration equipment, industrial and municipal wastes and wastewaters can also emit significant amounts of heavy metals compounds.

The transport (annual emission over 28000 t), industry (about 600 t), wastewaters discharge and disposal of pesticides are the main sources of environmental pollution with heavy metals in the region of Bukovyna [3].

The regional center for soils' fertility protection and control of the production quality carries out regular control of heavy metals content in the soils of Bukovyna. The analysis results have proved that this content complies with current requirements (see Table 1).

Table 1

Total content of heavy metals ions in the agricultural soils of Chernivtsi region, mg/kg

Upper layer (0 ÷5 cm)	Pb	Cd	Cu	Ni	Cr	Zn	Mn
Average content in the region	9.6	0.36	30.4	30.5	72.0	78.3	973
Range of concentrations within the region	3.0 ÷ 32.0	0.29 ÷ 0.82	12.0 ÷ 40.0	12.0 ÷ 50.0	32.0 ÷ 200.0	20.0 ÷ 100.0	500 ÷ 2000
Average content in the city of Chernivtsi	51.3	0.3	79.2	25.3	41.0	73.4	654
Range of concentrations within Chernivtsi	3.0 ÷ 32.0	0.29 ÷ 1.4	5.9 ÷ 40.0	12.0 ÷ 50.0	32.0 ÷ 200.0	3.6 ÷ 100.0	500 ÷ 2000

Higher content of lead has been identified for some spots near main roads. Higher content of copper has been determined in the soil samples taken from orchards. This can be explained by the influence of plants' treatment with some pesticides.

No local areas with excessive heavy metals pollution resulting from the industrial activity have been identified. The heavy metals content in the soils of Prykarpattya region and Prut-Dnister upland complies with the background values and can not threaten normal quality of the agricultural products [4].

It should be emphasized that the content of manganese in the soils of Bukovyna is higher comparing to other metals.

This is an important feature because the compounds of manganese are widely used in engineering and medicine and sometimes may have poisoning effect. Manganese can often be produced from its ores and minerals: pyrolusite, manganese (IV) oxide. The technology of pyrolusite processing requires its grinding, which produces a lot of fine dust. Inhalation of the dust may lead to serious poisoning. The normal content of manganese in the cell tissues is very low [2].

Manganese compounds have strong protoplasmatic toxic effect and affect the central nervous system, kidneys, lungs and the blood circulation organs. Even excessive throat/mouth washing with potassium permanganate solution may cause edema of vocal cords and mucous coat of mouth and throat. The ingestion of concentrated potassium permanganate solution may result in the stomach wall perforation. The ingress of manganese compounds into the urinary bladder or uterine cavity causes peritonitis [2].

The highest accumulation of manganese compounds in the human body is registered in liver. Urine and digestive system are the main ways of the manganese compounds excretion. Massive burns of gullet and degenerative changes in the parenchymatous organs have been reported after autopsy of the manganese pollution victims [2].

Plants accumulate manganese mostly in their roots. The accumulation coefficient is 62,0÷86,0 % comparing to the content in the soil (see Table 2).

As seen from Table 1, the distribution of manganese among parts of the corn can be represented as follows: stems contain 1,1÷4,5 %, leaves – 6,5÷30,8 %, coats – 2,1÷3,8 % and grains – 0,7÷1,4 %. Therefore, we can arrange the parts in the descending line based on the content of manganese:
roots>leaves>coats>steams>grains [5].

Table 2

Content of manganese in different parts of corn and for growing at different distances from the roads

Distance from the road, m	Content of Mn^{2+}, µg/g (for the dry weight)					
	soil	root	stems	leaves	coats	grains
>5	360	144	8	21	5	2
25	375	165	6	12	4	1
50	345	139	3	54	5	1
100	300	116	3	54	5	2
150	285	175	2	58	5	1
200	225	120	2	59	7	2

Plants require manganese to ensure normal processes of growing and cell breathing. This element also plays an important role in photosynthesis. The ion of manganese works in many ferments such as in oxydase. It acts as a reducing agent in the process of nitrate feeding and as a strong oxidizer in the process of ammonium feeding.

Manganese toxicity has been reported for the plants, which grow on acid soils [6]. High concentrations of manganese affect the normal development of roots and decrease the productivity of synthesis of chlorophyll. High concentration of starch, phenolic compounds and nitrates can worsen nitrogen metabolism efficiency for the manganese-affected plants.

Incorrect management with dangerous industrial waste materials can bring another potential threat for plants' growth and soils' quality. 225,7 t of such dangerous materials have been formed at industrial units in the region of Chernivtsi in 2007 [7]. This is more than it was formed in 2006 (180,4 t).

There were 40,1 t or 17,8 % of the first risk class materials (threshold limit concentration – 0,1 mg/m3); 81,6 t or 36,1 % of the second class materials (0,1÷1 mg/m3) and 104 t or 46,1 % of the third class materials (1,1÷10 mg/m3) among all the wastes collected in 2007. As seen from this distribution, an amount of the most environmentally dangerous wastes was the lowest. The wastes were mainly formed in the city of Chernivtsi, then in the districts of Novoseytsya (12,3 t) and Khotyn (11,5 t).

The total amount of the most environmentally dangerous wastes is gradually decreasing. This amount was 74,2 t at the beginning of 2008 or 22,1 % lower compared to the beginning of 2007. Only 17 t or 23 % of this amount is classified as the first risk class materials. Again, most part (69,9 %) of the waste materials are collected in the city of Chernivtsi, then in Novodnistrovsk (9,5 t) and in the district of Putyla (9,2 t). Novodnistrovsk is an area of construction of the Dnister hydropower and energy accumulation plant and the local wastes resulted from this activity. The district of Putyla is located in mountain area. Local anthropogenic activity mostly deals with the primary wood processing. Therefore, the wastes mainly consist of wood chips and other wood processing byproducts, which can not bring any serious environment threat.

All environmental dangerous materials have been removed from the storage facilities in the agricultural districts (Vyzhnytsya, Hertsa, Kelmentsi) of the region in 2008.

The decrease in amount of the environmental dangerous wastes of I-III classes collected in various industrial storages is shown in Fig. 1.

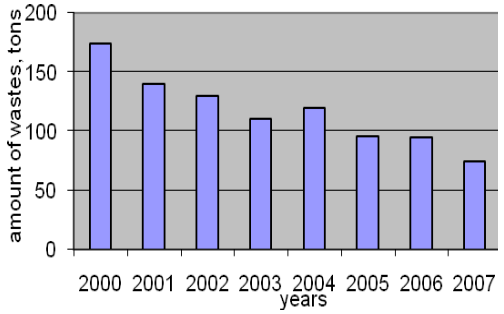

Figure 1. Changes in amount of the I-III classes wastes collected in the region of Chernivtsi in 2000 – 2007.

There is a significant part of metal compounds among the waste materials collected in the Chernivtsi region. The total amount of metals is estimated at 17,6 t and lead and chromium compounds constitute 86,2 % of all metal wastes. Lead is present mainly in old car and other batteries. There are also 2,2 tons of old luminescent lamps, which contain mercury. Such dangerous wastes can be utilized only outside the region.

The changes in the amount of the most dangerous 1 class wastes are shown in Fig.2.

The amount of stored prohibited and old pesticides and other agricultural chemicals is continuously decreasing. In the year 2008 this amount became 18,2 times lower than in 2007. There are only 1,4 tons of these chemicals remaining in the region.

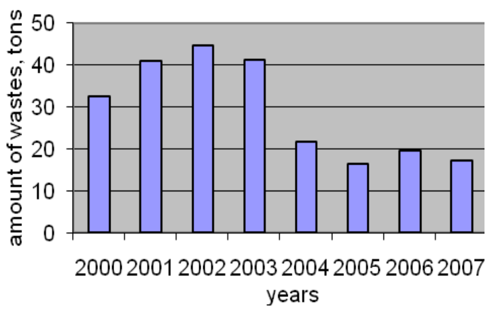

Figure 2. Changes in amount of the 1 class wastes during 2000÷2007 years.

Many various factors such as growing conditions, methods of processing can influence the content of heavy metals in food. On the other hand, different plants can uptake different amounts of heavy metals from the environment. The redistribution of heavy metals among different plant organs can also influence their final content in the tissues. Some cultivated plants can be placed into the following sequence according to the increasing ability to accumulate heavy metals: beans < oats and rye < barley < corn << cabbage < melons < potato < radish < onion < carrot < red beat << squash < cucumber < tomato << parsley < dill < onion leaves < spinach < lettuce [8].

There are two ways of heavy metals' salts ingression into plants: apoplasmatic and symplasmatic. This leads in general to the tendency of decreasing of heavy metals content in the row: root > stem > leaves > seeds [8].

The size of vegetables is an important factor influencing the content of heavy metals. The larger is the vegetable, the higher is heavy metals accumulation value [8].

Biocleaning of soils by planting some agricultural species is very interesting and an important field. For example, corn can actively accumulate heavy metals [5] and this plant can facilitate in the soils biocleaning.

Lead is mainly accumulating in roots and this tissue can accumulate up to 63,0-81,0 % of the total lead in the plant. The lead content in stem is much lower (3,8-10,1 %), in the leaves – 4,8-19,0 % and in the coats – 6,2-13,2 %. It is needful to emphasize that lead can ingress into leaves and coats mainly from the air. Only traces of lead were found in the corn grains. An average concentration of lead in the corn leaves was 4,9 mg/kg [5]. This is lower than the threshold limit value for the cattle feed (5 mg/kg).

Contamination with lead is irreversible, i.e. this pollutant is gradually accumulating in the surface soil layer even at very low and gradual ingress. The dependence of lead contamination on the distance from roads is nonlinear. Roadside forest shelter belts can capture some amount of the metal and prevent its spreading in the nearest roadside area. On the other hand, air fluxes can spread lead-containing dust over the belts at a longer range, which causes the highest content of lead in the soils at about 100 m from roads [9]. A content of lead in 100 m from the road was found 2,2 times exceeding its limit threshold value, in 50 m – 1,2 times higher. Related exceeding over the background content were 26,8 and 14,4 times. Similar spatial distribution has also been determined for cadmium. Its content in 100 m from the road was 1,5 mg/kg or 15 times over its limit threshold value [9].

The high content of cadmium has also been determined in the corn roots. Its concentration was several times higher than in the soil. The root barrier prevents further distribution of the metal towards the vegetation and reproductive organs. That is why its content in the stem and leaves is much lower and in the grains it is only at the trace level [10].

The accumulation of copper in the plants tissues is about 34,0-42,0 of the concentration in the soil. The stem of corn accumulates 8,4-13,5 % of the total copper accumulated in the plant; leaves – 20,3-28,6 %; coats – 12,7-21,1 % and grains – 9,9-18,4 % [5].

Copper is less labile element as compared to other ones. The most part of copper stays in the root and leave tissues until they die off and only very small part of the metal can get into new tissues. Copper is a vitally needful microelement. Unlikely to lead and cadmium it is required for normal plants' growth. On the other hand, the exceeding concentrations of copper cause hard intoxications which result in chlorosis and defects of the root system.

It is hard to foresee, which concentration of copper can cause toxic effect on plants. It should be remembered that the food manufactured from metals-contaminated plants can become dangerous even before having affected plants by poisoning and drop in the crop yield should be noticed.

Natural accumulation of heavy metals in some plants can be used for the phyto-rehabilitation of the contaminated soils [11, 12]. This problem has been extensively investigated by Galiulin et al [11], who proposed the use of chelate compounds of etylendiamintetraacetate (EDTA). Chen [13] proposed to use citic acid. Kravets [14] reported higher mobility and accumulation ratio of the mineral pollutants for the plants exposed to the non-specific stresses (presowing irradiation, deviations from the optimal growing conditions; too dense sowing). This effect can be useful for more intense phyto-rehabilitation.

Biomass of the phyto-rehabilitation plants can be utilized for the bio-fuel production [15]. Some non-ferrous metals can even be cost-effectively extracted from this biomass [16].

It is recommended to keep growing the food vegetables not closer than 150-200 m from the roads. Highly accumulating plants are not recommended for growth on metals-contaminated soils. Regional educational programs should promote more active testing of the metals content in some domestic cultivated plants in specialized laboratories. Special legislation regulations should prevent the growth of food plants at dangerous distances from roads while the increase of the ecologically clean products should be encouraged and stimulated by various means. Ecolabeling standards should be widely introduced. In this way a potential consumer would be able to see more adequate picture of the foods ecosafety and can make a well-grounded decision of buying needful foods. Special "green" shops, which work only with ecologically safe and clean products, can be recommended in a more distinct prospect.

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