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# RESEARCH OF MIGRATION PATTERNS OF HEAVY METALS IN THE SOIL ENVIRONMENT IN THE AREA OF PHOSPHOGYPSUM STORAGE INFLUENCE

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**Abstract.** The paper is focused on the research of migration process of heavy metals in the soil environment in the area of phosphogypsum storage in Sumy region. In the profile of the gray forest soils the corresponding genetic horizons were identified. The various structures of compounds containing heavy metals were detected in the samples by the diffractometric analysis. The increased gross content of lead in comparison with the background concentration in allocated humus and illuvial horizons has been determined.

**Key words:** phosphogypsum, migration, heavy metals, soil, genetic horizons.

## 1. Introduction

The risk of entering environment (E) pollutants during the placement of waste dumps from chemical enterprises causes a need to understand the ways of contamination E, distribution in the profile of migration in the soil, impact on plants, and ultimately, on human health [1]. The main source of E contamination in the areas of placement of mineral fertilizer production on the territory of Ukraine (Armyansk, Sumy, Rivne, Vinnytsia, Kamyanskoye) are arrays of phosphogypsum dump. In particular, Sumy region has already accumulated more than 14 million tons of this waste of different genesis: phosphorite and apatite phosphogypsum.

In the areas of phosphogypsum accumulation, heavy metals (HM) as a result of washing from dumps and accelerating migration under acidic conditions are subjected to horizontal and vertical redistribution by the soil profile, which may lead to their further migration into aquifers.

## 2. Materials and methods

### 2.1. Review of the previous research

The factors contributing to migration of pollutants can be: filtration of atmospheric precipitation through the soil layer, capillary rise of moisture to the surface of the soil as a result of evaporation; diffusion of adsorbed and free ions of soil solution; transferring colloidal particles on the surface; carrying over the root systems of plants; settling on natural geochemical barriers or barriers that arise as a result of anthropogenic impact on E, etc. Processes that promote migration of substances in soils in natural conditions are different in nature and the degree of influence. Often, speed, direction and magnitude of migration depend on season, time of the day, initial conditions and soil properties such as granulometric composition, soil medium reaction, organic matter content, and temperature of individual horizons.

Among HM, which pollute soil of phosphogypsum dumps, the most dangerous are lead and cadmium (first class of danger). Usually in soils involved in agro-culture, gross cadmium content does not exceed 1 mg/kg, while in contaminated areas its concentration is much higher, to 3 mg/kg of soil. Gross lead content reaches 20 mg/kg of soil at a maximum allowable concentration 100 mg/kg.

HM distribution in soil, absorption or accumulation of plants depends on the type of soil, its physical, physical and chemical properties, content of organic matter, redox conditions, antagonism or synergism between metals, their amount in pedosphere, soil temperature, vegetation type, etc.

In world practice, handling with phosphogypsum wastes is widely used in their storage in dumps.

Consequently, multi-year monitoring researches are carried out in the areas of formation of phosphogypsum dumps. Thus, in Florida Institute of Phosphate research (USA) [3] it was substantiated that the major changes in the area of phosphogypsum arrays accumulation can be characterized as a change in pH (from about 6.5 to 2.5), an increase in a number of soluble ions, especially sulphate and phosphate, inclusion of other ions such as chloride, fluoride, HM and radionuclides, and an increase amount of dissolved silica. Increasing concentration of many ligands leads to significant changes in predicted equilibrium of compound formation. Fluoride from stock solutions dumps can significantly affect modification of aluminum silicon and iron. The second major effect is appearance of ground water saturation with various solids. Low pH of contaminated solutions usually indicates that in most fresh water a part of solids falls into precipitate.

Monitoring researches of phosphogypsum dumps in India [4] indicate the development of water erosion phosphogypsum arrays, which can create cavities and instability solutions in the built dams, cause an increase in the surface runoff from dumps containing fine particles of phosphogypsum, erosion around the pipeline systems. Slopes can become more susceptible to failure and erosion with intense atmospheric precipitation.

Thus, the research of patterns of pollutants migration is relevant, in particular HM in natural components of E within the limits of possible influence of phosphogypsum dumps, which has its specific features of physical and chemical and biochemical transformations in accordance with territorial location and meteoclimatic factors, taking into account the genesis of phosphogypsum, which are superimposed on general regularities of the transformations of these substances in biogeochemical cycles.

According to the importance, the purpose of the work was the research of HM migration process on soil profile in the area of active phosphogypsum dumps in Sumy region.

## 2.2. Method of conducting field research of phosphogypsum storage area

The use of field methods allows us determine the structure of phosphogypsum dump – the boundaries of location breeding zones, the height of terraces, the area of the dump, to estimate the parameters of its spatial location in natural landscape, as well as possible directions for impact on natural objects and settlements.

Laboratory methods were oriented on establishment of laws of changing properties of phosphogypsum, depending on various factors that determine its physical and chemical characteristics such as elemental composition, chemical and mineralogical composition, acid-base balance.

Laboratory soil samples for the analysis of HM migration from phosphogypsum into E were selected and conducted.

X-ray diffraction was used to determine the structure of material performed on the automated diffractometer DRON-4-07 based on SumDU (sensitivity of measurements is at the level of 0.1 %). When removing the structure of sample material, CuK radiation (wavelength 0.154 nm)and Breg-Brentano focusing $\theta$-2$\theta$ (2$\theta$ – Breg angle). were used Current and voltage value on X-ray tube set 20 mA and 40 kV. Shooting samples performed in continuous recording mode (speed $1^o$/60 seconds), the range of angles 2$\theta$ from $15^o$ to $105^o$.

Elemental analysis of the samples was carried out on the X-ray fluorescence analyzer Elvax (Ukraine), based on SSU. Accuracy of determination of mass metal particle in the alloys is from 0.1 to 0.3%. The limits of HM impurities detection in a light matrix is not less than 10 ppm.

Measurements of pH of water extracts of phosphogypsum and soil samples were carried out in laboratory using pX-150 (ionometer) (Belarus) with glass combined electrode “EKS-10603”.

Removal of HM moving forms was carried out using ammonium acetate buffer. The content of Pb and Cd in soil solutions was determined by the atomic absorption method.

Phosphogypsum samples were taken from the dump and adjacent areas according to standard methods [5–7].

Sampling points were located on the territory of the dump and in adjacent areas, including sanitary protection zone of the dump, and beyond it. Phosphogypsum samples were taken from different sides of the dump from each terrace level, thus samples differed in terms of storage time and depth of occurrence. On re-cultivated slopes phosphogypsum samples were taken under the pre-exposed soil layer.

Soil samples were taken around the dump up to 200 m from the dump at equal intervals 50 m apart, as well as on soil profile to the soil forming rock every 10 cm. Soil samples after removal were dried under standard conditions (pressure 1 bar = 105 Pa = 750.06 mm Hg, temperature 298.15 K = 25 °C) and powdered.

As priority climatic criterion of water supply resources, nature and energy of soil formation and soil fertility for zoning forest-steppe territory, the relative indicator – hydrothermal coefficient of Selyaninov (GTK) is used, which is the ratio between the amount of precipitation in the period when the air temperature is above 10 °C, and the sum of indicated temperatures for this period, multiplied by 10 [8].

### 2.3. Characteristics of soil profile near the phosphogypsum dump

On a larger area of the territory around the phosphogypsum dump, a gray type of forest soils, which is characterized by loose, granular, densely penetrated roots of plants, with a humus and accumulative horizon (humus content from 3–4 % to 6–8 %) was naturally formed, which is the manifestation of advantages of the sod process.

The soils are characterized by an acidic pH on average 5.8 to 6.5 units, absence or disguise of transient horizons on the soil profile weakly – expressed eluvial and well – expressed illuvial horizons of fulvous brown color. Beyond the sanitary-protective dump zone, there is farmland where the upper soil horizons, first of all, humus-accumulative and a part of eluvial one, are plowed. All subtypes of gray forest soils on this territory are combined by acidic reaction in upper horizons, unsaturated bases and low nutrient content. It is believed that this group of soils has some unfavorable physical properties, and, first of all, weak structure.

Fig. 1 shows a photo of a soil profile section at the sampling site for analyzing contents of HM near the phosphogypsum dump.

**Fig. 1.** Profile of gray forest soil near phosphogypsum dumps

Soil profile was formed in places with minimal parameters GTK V-IX = 1,18-1,20, which are caused both by climatic factors and relief due to additional accumulation of waste water moisture to the values GTK V-IX = 1,76.

In the profile of gray forest soils near the phosphogypsum dump the following horizons are distinguished (Fig. 1): $H_0$ is dark brown turf (capacity up to 2 cm); H is humus cumulative with dark gray turf with silica powder (7–11 cm); $E_1$ – an eluvial one of grayish white colour, with powdered-lumpy structural composition with carbonate inclusions, contains many plants roots (18–20 cm); $E_2$ is transient eluvially-illiual plated nougat with carbonate inclusions, compacted; transition is gradual (6–10 cm); I is iluvial of brown colour lobed-prismatic (32–35 cm) and P is soil forming rock with a depth of 60–80 cm [10].

Significant factor is the presence in the soil of water-soluble, and therefore mobile, fulvic acids, which causes processes of intensive washing from the soil profile of many trace elements – Fe, Mn, Zn, Cd, Pb, Sr, V, including HM. This process is also characteristic gray forest soils.

Conducted diffractometric analysis soil data revealed the presence of various structures (oxides, sulfates, phosphates, carbonates), including those containing HM, in particular – Cd, Pb. In main phase of spectrum: $SiO_2$ silicon oxide, $Al_2O_3{\cdot}2SiO_2{\cdot}3H_2O$ aluminosilicate compounds, iron oxide FeO.

## 3. Results of field research of migration of HM in soil E in the phosphogypsum storage area

Monitoring research in 2017 showed some changes in radial distribution of lead and cadmium on the soil profile in comparison with previous field research in the area of active phosphogypsum dump in Sumy region [9, 10]. Comparative analysis was carried out on gross contents and moving forms of HM. On the dump territory the soil is characterized by increased values of total lead content ($Pb_v$) as compared with background concentration in isolated genetic horizons (humus and iluvial) (Fig. 2).

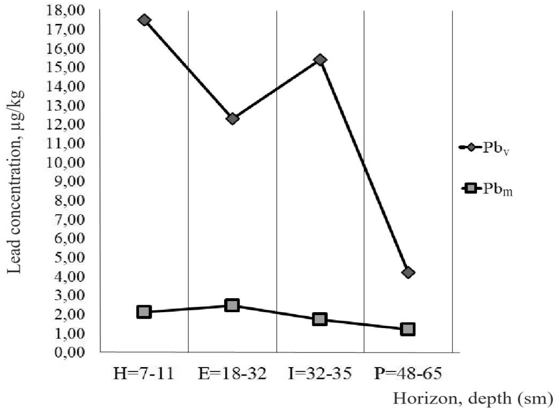


**Fig. 2.** Radial distribution of lead in the soil profile

Regarding lead moving forms ($Pb_m$), the highest values were noted in the upper 0-10 cm horizon and at a depth of 18 cm, which fluctuate between 3.5–1.76 µg/kg, then down the profile, there is a decrease in concentration to the level of 1.21 µg/kg with MPC = = 6 µg/kg.

In the upper horizon there was also cadmium accumulation the amount of which down the profile decreases to the illuvial horizon (Fig. 3).

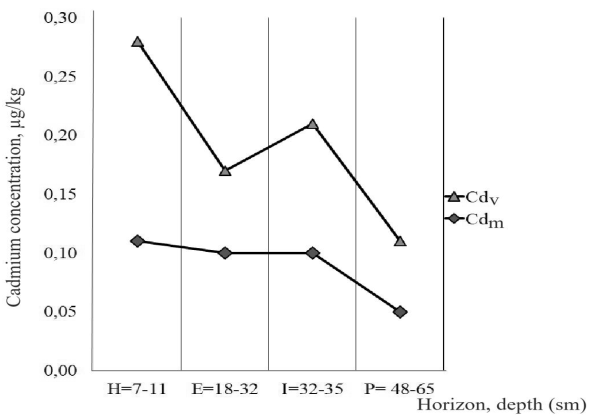


**Fig. 3.** Radial cadmium distribution in the soil profile

Total cadmium ($Cd_v$) content in the upper horizons remains approximately equal to 0.25–0.33 mcg/kg, then at a depth of 18–32 cm it decreases to 0.17µg/kg and at a depth of 32–35 cm. its concentration slightly increases. In the case of moving forms ($Cd_m$), their value is significantly less than MPC (1-2 µg/kg) with a gradual decrease in horizons within the range of 0.11–0.05 µg/kg.

## 4. Conclusions

The research describes the soil profile of the area of active phosphogypsum dump location. The conducted diffractometric analysis of soil data revealed the presence of various structures (oxides, sulfates, phosphates, carbonates), including those containing HM, in particular – Cd, Pb. In the main phase of spectrum there are: $SiO_2$ silicon oxide, $Al_2O_3{\cdot}2SiO_2{\cdot}3H_2O$ aluminosilicate compounds, and FeO iron oxide.

Comparative analysis of gross content and moving forms of HM in the soil on the dump territory is characterized by higher values of total lead content compared with the background concentration in isolated humus and illuvial genetic horizons. In the upper horizon, cadmium accumulation was also observed, the amount of which decreases to the illuvial horizon down the profile. Lead and cadmium concentration does not exceed the MPC, which is related to the possibility of absorbing these cations by soil complex of gray forest soils rich in clay minerals and humus, which causes soil to perform a buffer function to protect ecosystems.

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