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Ecological and geochemical study of the state of soil deposits in the impact areas of municipal solid waste landfills

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SUMMARY

As a result of the analytical research and result of the previous stages of study it was found the significant contamination of the soil layer by the heavy metals (HMs) within the Kyiv's Landfill area No 5 for the municipal solid waste (MSW) disposal and the surrounding areas to the north-east and north-west. It was revealed also the negative its effect on the contents of these pollutants in the soil of adjacent buffer zone. This is a result of almost 34 years of the operation of the MSW disposal facility, when there were operating troubles.

In order to measure the concentrations of the chemical elements in the soil samples such key methods as the atomic emission spectroscopy (AES) and inductively coupled mass spectrometry (ICP-MS) are used.

So, soil deposits of the Landfill have get the maximum exceed of background contents for cooper, lead, nickel, and tin by from several to ten times, at the same time, beyond its contour – by 2–3 times. The negative changes of physical-chemical properties of soils of the humus horizon is revealed by the comparison with the proper indications for the soil samples collected in the sites adjacent to the Landfill and directly on its territory. The buffer coefficient of soil of this horizon is twice as lower for the technogenic polluted soils within the MSW disposal facility than for the background sites.

The contents of mobile forms for the HMs in the soil formations of the Landfill No 5 in the comparison with the background values increase 2 times for cooper and zinc, as well 8 times for lead.

Introduction and problem definition. In Ukraine (except for data from the Autonomous republic of Crimea and the city of Sevastopol) for 2018 almost 54 mln m^3 of domestic waste or more 9 mln tons were discarded (State…, 2019). Most of them are deposited in 6,000 landfills and disposal sites with a total area of over 9,000 ha. At the same time, the number of overloaded landfills is 256 units (4.2%) and 1347 units (16%) do not meet the sanitary, hygienic, and environmental standards. Most landfills do not have the engineering and geological maintenance. As a result within both the landfills and in the surrounding areas the soil deposits, surface water, high groundwater zone are undergone the substantial technogenic changes that often leads to the drastic changes of the plant communities (Bauer et al., 1998; Aluko et al., 2003; Abu-Zeid et al., 2004; Słomczyńska and Słomczyński, 2004; Mor et al., 2006; Øygard and Gjengedal, 2009; Shevchenko and Medvedieva, 2010; Adeolu et al., 2011; Bhalla et al., 2013; Azimov et al., 2018a,b,c, 2019a,b,c,d,e; Trofymchuk et al., 2019; Kaliaskarova et al., 2019).

The physic-chemical processes of pollution for the environmental objects that is essential to human well-being at these areas are not yet in fully understood. In addition to, the soil formations are the most important biogenous and abiogenous deposit environment (Karmazynenko et al., 2014). The key role in physiological, bio- and geochemical processes, which proceed in the soils belongs to the heavy metals (HMs). They determine the optimal conditions for the existence of the living organisms in the soil and its biological productivity.

Consequently, this paper demonstrates the summarized data for the geochemical features of soil deposit samples, which are *the study object*. We collected the factual materiel both in June 2019 and during the previous years (Azimov et al., 2018a,b,c, 2019b,c,d,e) for a few test sites within the storage map No 1 of the *Kyiv's Landfill area No 5* of the municipal solid waste (MSW) disposal and for the adjacent areas to the north-east and north-west. The landscape components apparently of these buffer zones located beyond the Landfill area are exposed to the long-time influence of this disposal object, since it entered into service as far back as 1986 and now it has exceeded twice its capacity in the context of accumulation of waste (Azimov et al., 2018a).

The most test sites for 2019 match with the sites of soil cover sampling for the previous years. This is an element of geomonitoring. However, the additional data obtained in the buffer zone to the north-east from the Landfill area contour and in the area of the Pidhirtsi village, which is situated to the east from Landfill have been added to the generalization of material.

Also, the ***main problem*** of study is first of all to determine the maximum values for the different geochemical parameters of soil among all generalized data over the area the Section "A" of the Landfill and its buffer zone. The next step was the analytical comparison of these parameters with the same characteristics for the background soils, which are inherent in the region, where the Landfill No 5 is situated. As data of a comparison the estimations of the geochemical features of soil horizons for our landscape-climatic subzone – forest-steppe right-bank high (mainly) and low (partly) obtained by N.H. Lyuta (Lyuta, 2004) are used. The first step along this path was to definite the soil types and their main characteristics in the exposure (clearing) profiles during the field works and using the special thin sections prepared from the collected soil samples.

Characteristics of the study area. Landfill No 5 is situated approximately 11 km to the south from the residential and industrial development at the southern Kyiv. MSW is stored within two former left tributaries (the gullies of sub-meridian direction) of the Khodosivka's gully at river valley of Marusyn Yar (see Figure 1 in Azimov et al., 2018a). The gully stretched between the Pidhirtsi (at a distance of 750 m and Krenychi (at a distance of 500 m) villages.

As far as the technical characteristics of Landfill No 5 it should be noted that its overall area is 63.7 ha. It includes two sites (or Sections) for storage: Section No 1 (or "A") at the area of 18 ha and Section No 2 (or "B") at the area of 17 ha. The landfill receives from 4000 to 5000 m^3 MSW every day.

Since 2006 it is a question of the complete closure for the Landfill No 5 due to its critical ecological conditions that is related primarily to the leakage of the filtrate into the soil and environment and groundwater pollution. In fact, the formed aqueous solutions saturated with toxic pollutants are the chemically and biologically active. Nevertheless, exploitation of the Landfill is still ongoing.

Methodological part. To determine the features of HMs lateral distribution in soils at the studied area the samples from the surface soil horizons (0–5 and 5–10 cm) were collected by the “envelope” method in accordance with the requirements of GOST 17.4.4.02–84 (Environmental…, 2008). To study of the pollution penetration to a depth *in situ* the soil profiles are researched to 1.0 m. The sampling of the proper clearings is performed along the horizons at the sample collection intervals of 0.1 m.

The chemical element concentrations in the soil samples are determined using atomic emission spectrometry. Also, the ICP-MS ***method*** (inductively-coupled plasma mass-spectrometry) is applied to define the HMs speciation in soils. The physico-chemical properties of soil deposits are determined by the E.V. Arinushkina procedure (Arinushkina, 1970). The mineralogical content of soil fractions is measured using X-ray phase analysis by the Dron-2 diffractometer (Cuk_{α}-radiation).

When the chemical substances enter into soils in excess amount, the greatest danger is an increase in content of these moving forms. They can transfer in the media adjacent to the soil: namely underground and surface waters, plant communities. That is why the soil is a real threat for the natural functioning of the biogeocenosis.

The high values of moving microelement mobility record the chemical soil pollution. There are the different ways to classify the soils by their property to inactivate the HMs. As a criterion of quantitative ecological and geochemical estimation for the stability of “soil-solution” system and its impact on the arrangement of the mobile HM forms, a buffering capacity coefficient (C_b) for the humus soil horizon was used. This was developed by the group of the authors (Samchuk et al., 1998). This indicator is proportional to the sorption capacity for soil absorption complex (SC) and inversely proportional to the change of ΔpH in the “soil-solution” system:

$$C_b = SC/\Delta pH \tag{1}$$

The study of the HMs ***speciation*** in the soils was performed using the method of sequential dissolution developed by V.O. Kuznetsov and G.A. Shimko (Kuznetsov and Shimko, 1990) and expended by A.I. Samchuk (Samchuk et al., 1998). The method is based on the collective extraction of several elements from the soil using the “selective” extractants. The following chemical forms of HMs in soils are determined:

1) *Water soluble form.* Speciation of HMs, which allows the HMs transferring into aqueous extract.

2) *Exchangeable form.* The exchangeable ions are called the soil-retained ones due to the electrostatic forces and those can be substituted by an equivalent amount of the ions from the neutral solutions of neutral salts. It is represented by poorly absorbed HM forms associated with the hydroxide of iron, manganese, silicon, organic matter, clay minerals.

3) *The form associated with carbonates* consists of the HMs sorbed be the carbonates and isomorphic impurities.

4) *The form sorbed at the amorphous hydroxides of iron, manganese.* It is represented by the HM ions, which are absorbed by the hydroxides of iron, manganese. That is a set of forms for the metals, which are formed the surface complexes and pass into the solution when the hydroxides of iron and manganese are destructed.

5) *The form connected with the organic matter.* It is represented by the strong metal-organic complexes (the complex compounds of HM ions with the humic acids).

6) *The poorly soluble form* includes the metals, which are concluded into the crystalline lattice of rock-forming and accessory minerals.

Data of laboratory analyses relative to geochemical characteristics of soil samples from the studied area are compared analytically with the similar parameters for the background soils, which are typical for the area in question a whole (forest-steppe right-bank high). In this case the basis was taken the data are given (Lyuta, 2004).

Results and discussion. In order to estimate the ecological conditions of the **recent soils** during the joint field study within the Landfill area No 5 and in the range of its impact we have investigated three their sections for the three different clearings. Therefore, below we examine the characteristics of soil ***types*** that have been identified. The detailed morphological features of the recent soils in the sections (coloration, structure, granulometric composition, humidity, grain size composition, neoplasms, inclusions, horizon-to-horizon transfer, and boundary) allow distinguishing the types of these sediments.

Soils are primarily marked by the dark gray color of their profile, cloddy structure, and light loam granulometric composition with the vermiculations and molehills, neoplasms of carbonates as a mycelium and gradual transitions between the genetic horizons (H, Hk, PHk, Phk, Pk). According to these features the soils are close to *typical chornozems*, formed on the loess sediments of *Bug's time*. And these same loess sediments are use to cover and bury further the domestic wastes at the area of this Landfill No 5.

To define more exact the soil genesis and assess the extent of soil pollution the samples were collected for the micromorphologic analysis. The results of the micromorphologic analysis of the recent chornozem soils will allow not only assessing the extent of pollution (identifying the particles under a microscope), but also getting more accurate their genesis (for the correct application of measures aimed at the withdrawal of the pollutants and environmental improvement both the same sediments and the environment in whole).

The analysis of ***granulometric composition*** of soils from the aeration zone for the Landfill area No 5 shows that sand fraction, aleurite and clay fraction contents vary over the ranges 1–6%, 3–10% and 84–90%, respectively. Therefore, clay fraction is prevalent for the soil deposits at the area in question and serves as a main sorbent for the pollutants. The clay minerals for this fraction are montmorillonite, hydromicas (illite-like) and kaolinite.

The ***chemical composition*** of the soil samples range for SiO_2 from 49 to 82% and for Al_2O_3 from 4 to 8%. The soil samples collected directly *at the Landfill area* as a part of research have shown the maximum exceed for the background contents (after Lyuta, 2004) of microelements was recorded for such HMs as the followings: cooper, lead, zinc, nickel, and tin. In particular, zinc content in soils for the Landfill No 5 reaches 500 g/t at the background content of 48 g/t for the Dnieper forest-steppe geochemical province. Maximum cooper content reaches 600 g/t at the background content of 20 g/t, i.e. 30-fold excess of the background indicators are registered (Figure 1).

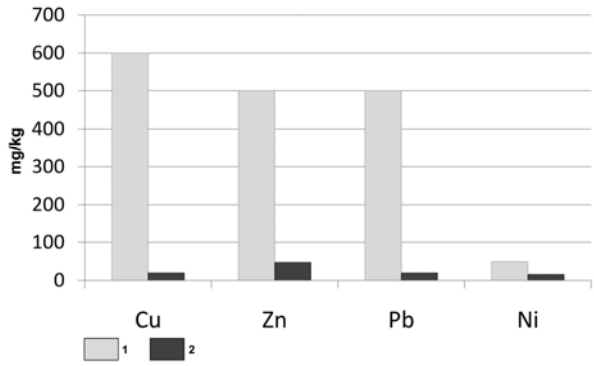

Figure 1 *Comparison of the maximum exceed for the heavy metals contents in the technogenic polluted soils for the area of Section "A" of the Landfill No 5 and in the background soils from the studied area (after Lyuta, 2004). 1 – heavy metals maximum contents in the studied soils of Section "A" of the Landfill, 2 – heavy metals contents in the background soils*

The highest lead content in the soils within the Landfill is 500 g/t that are 25 times higher than the background indicator (20 g/t). Here the high nickel content is recorded as 50 g/t at its background content of 16 g/t. The high tin content is also indicated that 20 times higher than its background content.

In the buffer zone of the Landfill No 5, namely in the region beyond of its borders, but such one which is undergone of Landfill impact the soil microelement contents are also 2–3 times higher than their background ones. This is true for cooper, lead, zinc, nickel, chrome, and tin.

Using the previous studies the ***physic-chemical properties*** data for the humus horizon are obtained as for the Landfill area as beyond of its contour. In particular, *beyond Landfill borders* the following indicators of soils are determined: $C_{org.}$ – 6.2%, pH 6.5; exchangeable cation content, mg-eq/100 g: 8.2 for H^+, 39.0 for Ca^{2+}, 12.8 for Mg^{2+}, 0.7 for K^+, 0.65 for Na^+; and total exchangeable cations is 61.35. At the same time, the physical-chemical properties of the soil collected *within the Landfill* are differed from the values mentioned below that pointed at their changes: $C_{org.}$ – 3.6%, pH 6.3; exchangeable cation content, mg-eq/100 g: 3.2 for H^+, 12.0 for Ca^{2+}, 4.9 for Mg^{2+}, 0.3 for K^+, 0.4 for Na^+; and total exchangeable cations is 20.8. Without any doubt the mentioned changes are caused by the action of different toxicants connected with the activity of MSW disposal facility.

The findings allow the calculating ***buffer coefficient*** for the humus horizon soils using equation (1). So, the estimate for buffer coefficient of soils *beyond the Landfill contour*, which are under the influence of its north-eastern, northern, and north-western parts, is equal to the value of C_b=55. For the technogenic polluted soil formations within the *Section "A" of the Landfill* the value of C_b decreases almost twice.

The ecological and geochemical estimation of the impact of the Landfill for SMW disposal on the conditions of soils here have been produced under these studies. For this purpose the ***occurrence forms of HMs*** in soil cover of the *Landfill*, which are in excess of the similar background values, are determined, i.e. lead, zinc, and cooper. As a result of the performed analytics it was found that the contents of the mobile forms (water soluble and ion-exchangeable) in soil formations, which most influence the environmental assessment of the territory, increase, i.e. for cooper and zinc – twice, for lead – in 8 times. It is the content of the mobile forms that affects the migration of the HMs in the trophic chain "soil–solution–biota".

Hence, the comparison of geochemical features for the samples of technogenic polluted soils from the Landfill and adjusted areas with those for the samples of background soils allows for the following conclusions. Since putting into service in 1986 the MSW disposal Landfill No 5 due to the improper its operation that caused by the breach of operating procedures of the covering the garbage storages by the isolating layers of dirt, intermittent work of the leachate treatment system, capacity exceeded, etc. the soils within its boundaries and also in the buffer its zone have been contaminated by the different toxic substances, in particular by the HMs.

It is worth noting that in the last years the Kyivspetstrans Joint-Stock Company, which delivers the MSW disposal services, takes on the task of improving Landfill safety and preparation for its reclamation. There are the remediation of dangerous slopes for the Section "A", capacity addition for the leachate treatment, reinforce and modernization of the protective dams (especially a dam located to west from the Section "B"). As a result, the transfer the pollutants from the Landfill area beyond of its boundaries and negative their impact on the environment components are slowly decreased. This is recorded by our studies (Trofymchuk et al., 2019; Azimov et al., 2019a).

Conclusions and prospects for the further studies. As a result of the analytical research and result of the previous stages of study it was found the significant contamination of the soil layer by the heavy metals and above all within the Landfill area No 5. It was revealed also the negative its effect on the contents of these pollutants in the soil of adjacent buffer zone. This is a result of over 33 years of the operation of the MSW disposal facility, when there were operating troubles.

So, soil deposits of the Landfill have get the maximum exceed of background contents for cooper, lead, nickel, and tin by from several to ten times, at the same time, beyond its contour – by 2–3 times. The negative changes of physical-chemical properties of soils of the humus horizon is revealed by the comparison with the proper indications for the soil samples collected in the sites adjacent to the Landfill and directly on its territory. The buffer coefficient of soil of this horizon is twice as lower for the technogenic polluted soils within the MSW disposal facility than for the background sites.

The contents of mobile forms for the HMs in the soil formations of the Landfill No 5 in the comparison with the background values increase 2 times for cooper and zinc, as well 8 times for lead.

In order to elucidate the mechanism of pollutant migration in the environment components for the area in question (soils–natural water–vegetation) it needs to carry out their ecological-geochemical sampling over the regular network of land-based sites. The basic necessity is to focus efforts of the specialists on the seasonal assessment of Landfill impact on the environment conditions as a whole.

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