# Environmental pollution with heavy metals: case study of the household waste

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**Abstract.** This study is dedicated to the assessment of the heavy metals pollution of environment through analysis of the heavy metals sources and the measuring their concentrations in leachate and soil near landfills. Main sources of heavy metals in the household waste are identified. The environmental pollution with some heavy metals (Cr, Pb, Cd, Ni) was assessed. Soil contamination by heavy metals near the landfills was analyzed by measuring their concentrations in the soil on different distances from the landfill. The limit exceeding was not observed for any heavy metal. Only cadmium has demonstrated a strong correlation between the distance from the landfill and the concentration. The research also confirms depending of heavy metals migration on the landfill conditions and on its compliance with requirements. Also, heavy metals concentrations are defined in the leachate collected using the landfill-simulating reactors. Heavy metals content was identified as high. Higher concentrations are found where more organic fraction is present in the waste. There are conditions inside the reactors, especially acidity, which are crucial at the early stages. Further, a significant impact can be caused by unequal distribution of heavy metals in the waste body. Due to accelerated water regime in the reactors, the heavy metals concentrations in a landfill leachate are predicted up to 50-55 years. Forecast shows multiple (2-18 times) exceeding the allowable concentrations of all heavy metals, even after long-time landfill usage.

**Keywords:** heavy metals, pollution, household waste, landfill-simulating reactors, landfill.

# 1    Introduction

One of the most widespread environment pollutants are heavy metals. Sources and ways of heavy metals emission into the environment are manifold. In many regions, due to the absence of industry plants, one of the main heavy metals source are landfills. Landfilling is still the main method of the household waste handling in developing countries. Besides, these countries mostly do not have waste separation system. That is why a lot of hazardous substances are delivered to landfills as well. Taking into account the poor conditions at landfills, there is a real threat of such substances migration into the environment. Usually, some part of the mobile forms of hazardous substances migrates from the landfill to the nearby soils. A big part of heavy metals at landfills moves to a soil which is a powerful accumulator. Heavy metals are known as main soil pollutants after waste landfilling. The contamination may not be noticed for a long time due to a high buffer capacity of the soil. The authors [1] consider heavy metals as main soil polluters near landfills. Soil contamination by heavy metals near landfills was studied by many authors [2-6]. In many countries it is obligatory to control some parameters, including heavy metals, in soil near landfills. Therefore, a research of hazardous substances concentrations in soil near landfills is the important task. Also, high heavy metals content can be found in landfill leachate. If taking into account potential environmental pollution with heavy metals, an extra hazard is caused by hazardous components of the household waste studied by the authors [7-9].

Heavy metals migration in the soil is conditioned by many factors: reduction-oxidation, acid-basic soil properties, organic content, granulometric composition, water and heat regime, geochemical properties, and other. Heavy metals can move in the soil with liquid and suspension, plant roots or soil microorganisms. Heavy metals migration with surface water is mainly occurred in suspended form. Water contamination by heavy metals can be also assessed using bioindication, as reported in [10-13].

The authors [14] indicate that majority of the heavy metals compounds are not decomposed by microorganisms and chemicals. Therefore, their total concentration in the environment remains stable for a long time.

One should note heavy metals predisposition to accumulation in the environment, but not decomposition unlike many other pollutants [15]. It is known [14] that the form of the environment contamination by heavy metal depends primarily on the type of process of its formation. The content of every heavy metal and its physical and chemical properties are also influenced by the way of waste treatment (recycling). Besides, subsequent heavy metal influence and its dissemination depend on the soil conditions, the chemical composition of groundwater and the existing migration mechanisms in the environment.

The total heavy metal content in the environment does not fully reflect its danger to the environment. The more important is the available (mobile) content. This is the part of the total heavy metal amount, which can migrate to the environment or be absorbed by living organisms [16-19].

Authors [20] have also concluded that long-term impact of landfills on the environment (including the potential heavy metals release from landfill body) is not completely known. It is known that small quantity of heavy metals is leached from the landfill body [21,22]. The release of heavy metals from landfills can last hundreds of years, creating a large potential risk to future generations.

Therefore, the goal of this study is to assess the heavy metals pollution of environment through analysis of heavy metals sources and the assessment of their concentrations in leachate and soil near landfills.

## 2    Sources of heavy metals

Heavy metals are often found in the household waste as part of used electric devices, batteries, paints, different plastics, etc. They are also accumulated in ash and slag of waste incineration plants. The content of Zn, Pb, Cd, and Cu is the highest in such an ash [23]. Heavy metals concentration is even higher in a volatile ash: As – up to 230 mg/kg, Cu – up to 1300 mg/kg, Pb – up to 8300 mg/kg, Zn – up to 27000 mg/kg [16]. Besides, a high content of heavy metals (primarily Pb, Ni, Cd, Cr, Cu, Zn) is found in sewage sludge, including those from household dwellings. According to [14,24] more than 30% of that sludge is often used then as fertilizers for agricultural land, which leads to further heavy metals migration to the environment. The significant source of heavy metals, especially in rural regions, is waste of pesticides use. It contains, for example, lead arsenate ($AsHO_4Pb$), "paris green" copper acetoarsenite ($Cu(C_2H_3O_2)_2 \cdot 3Cu(AsO_2)_2$), bordeaux mixture ($CuSO_4 \cdot 5H_2O + Ca(OH)_2$), copper oxychloride $3Cu(OH)_2 \cdot CuCl_2$) and phenyl mercuric chloride ($C_6H_5ClHg$) [16,25].

Based on the analysis and taking into account other numerous studies [15,16,26-33], the sources of the most widespread heavy metals delivering into the environment as a part of waste were summarized as follows:

Pb: cement, pesticides, paints and pigments, enamels, varnishes, dyes, catalysts, batteries and accumulators, printing products, TVs and other electrical devices, fluorescent lamps, colored glass, ammunition, construction waste, waste of vehicles (tires, engines), metal products (lead-asbestos plates, anticorrosive containers, anti-radiation screens), technical oils, sewage sludge, ash of coal and waste incineration, plastic waste.

Cd: batteries and accumulators, electrical cables, car radiators, cement, waste of pesticides and fertilizers use, PVC-plastic, colored glass, paints, glues, waste solar panels, ash of coal and waste incineration.

Ni: batteries and accumulators, cement, pesticides, old vehicles, sewage sludge, catalysts.

Hg: thermometers, fluorescent lamps, batteries, dyes, PVC-plastic, pesticides, paints, printing products, TVs and other electrical devices, accumulators, barometers, manometers, ash of coal and waste incineration.

Cr: cement, varnishes, paints and pigments, dyes, batteries, printing products, waste electronic devices, metal products made from stainless steel.

Zn: cement, pesticides, paints, waste medicines, batteries and accumulators, fluorescent lamps, waste of office supplies, construction waste, ash of waste incineration.

Cu: electrical cables, cement, car radiators, pesticides, coloured glass, paints, varnishes, dyes, printing products, sewage sludge, ash of waste incineration, agriculture waste (livestock).

As: paints and dyes, waste medicines, pesticides, printing products, ash of waste incineration.

Lead is used in paints, printing alloys, solder, accumulators, various metal products, chemicals and dyes, as building material and for casting [29]. Also it is widely used in the soundproofing materials. High corrosion resistance causes its application in the constructions. The use of lead in decorative paints production (lead white and coloured paints) is noticeably reduced, but the production of lead sulfur and lead chromate remains intensive due to their low cost and good anti-corrosion properties. Lead is also used in the automobile wheels. The use of lead-porcelain enamels for aluminium coating and radiation-protection screens constantly increase. Organometallic compounds of lead are used in paints, antibacterial agents and various pesticides. Lead is delivered to landfills also in the form of dyes for glass (lead (II) oxide strengthens the colour of glass and gives bright hues). Also, the source of Pb are stibium-lead batteries (in the form of $PbSb_2O_6$).

Cadmium is applied to products to provide a gloss and corrosion resistance. These products include, for example, details from car, radio and television equipment, household appliances and other metal products. One of the main cadmium sources in the soil is the waste of fertilizers use [27]. First of all, these are phosphate fertilizers, where its concentration can reach more than 100 mg/kg according to [16]. Cadmium is also used in packaging materials (except food). Cadmium sulfides (orange-yellow colour) and cadmium sulphoselenides (pinkish-red and chestnut colours) are used as dyes in plastics, ceramics, paints and coating materials. Cadmium pigments are used for colouring vehicles. Cadmium stearates are used as stabilizers in polyvinyl chloride plastics (PVC-plastics). However, cadmium-based stabilizers are not used in flexible PVC-based plastics for food products packaging because of the potential danger of contamination. Cadmium is also widely used in accumulators due to the high degree of electrochemical reactions reversibility in a wide range of temperatures, low discharge velocity and the simplicity of battery recharge. These batteries are used in different appliances: in electric toothbrushes and razors, other electric tools (drills, scissors, etc.), medical devices, mobile phones, emergency light sources. There are constantly increasing emissions in the residential sector due to the intensive use of washing detergents which contain cadmium in households. Other areas of cadmium use: cadmium coatings of fluorescent lamps, X-ray screens, phosphorescent labels; cadmium alloys in cadmium-silver solder, automatic fire suppression systems, valve gaskets of high pressure gas cylinders, in transport and telephone wires, car radiator grates; electrical and electronic devices: relays, switches, car interrupter contacts, solar panels [28,29]. The majority of nickel is delivered into the waste as inert form of alloys (first of all, stainless steel and steel alloys) and with used products having galvanic coating. Among the industrial waste containing stainless steel with nickel there are scrap metal and equipment (parts of cars, electrical equipment, construction waste, tools, etc.), used solar panel elements. Pure nickel can be emitted to the environment with used household appliances. One of the major sources of active (available) nickel compounds is nickel-cadmium batteries for various power sources and zinc-nickel acid accumulators [29]. Nickel along with lithium-ion batteries gets to the environment most often in the form of $LiNiO_2$. Besides, nickel-chrome alloys a log time have been used in household heating appliances.

Chromium is mostly contained in household waste inside used power supplies and residues of paint and varnish materials.

The majority of mercury is accumulated in water bodies with about 0.1% remaining in dissolved form. Moreover, the author [34] points out that the highest mercury inflow into the environment takes place in economically less developed areas. The use and further recycling of mercury-containing devices is the main human source of mercury. Significant mercury amounts are also delivered into the environment with waste of research equipment, fluorescent lamps, and with amalgam waste in dentistry [28].

Zinc-containing wastes are accumulated from natural and synthetic rubber (zinc oxide is used as a catalyst for vulcanization), dry batteries, lithographic plates, roofs, paints, paper, cosmetics, medicines, and agriculture [29]. The new powerful source of zinc is old nickel-zinc batteries used in the electric vehicles. Besides, as part of polymer waste there is zinc salts providing polymer protection from excess chlorine or chlorides formation. Zinc compounds are also part of various office equipment.

The main copper deliverer into the environment is electronic and electrical equipment and power supply equipment. Other sources include heat exchangers, wiring and winding in engines, transformers and generators [29]. Copper-containing pesticides were previously widely used, but now their use has decreased significantly and this source of copper in waste also reduces. Copper comes to household waste also in the form of copper (II) oxide in sodium-calcium glass (provides blue colour) and in potassium-zinc glass (provides green colour).

The main sources of arsenic compounds in the waste are as follows [29]: cement, medicines, pyrotechnics, hair removal means, enamels, pesticides (insecticides, herbicides, desiccants in the form of calcium arsenate or sodium arsenate, fungicides for wood impregnation), food additives, cleaning chemicals. Arsenic is also widely used in cosmetics. Relatively new strong source of arsenic in waste is electronic industry.

Heavy metals in different household waste types were identified by the authors: construction waste – Zn, Pb, Cu, Ni, Cr, Cd, As; expired medicines – Zn, As; PVC-plastic – Hg, Cd; pesticides / fertilizers – Hg, Cu, Pb, As, Zn, Cd, Ni, Mn; paints, varnishes – Pb, Cr, As, Hg, Cu, Zn; batteries – Pb, Cr, Zn, Cd, Ni, Hg, Cr, Hg; printing products – Pb, Cr, As, Hg, Cu; TVs – Pb, Hg; accumulators – Ni, Cd, Pb, Zn; electronic devices – Pb, Cg, Hg; fluorescent lamps – Hg, Cu, Ni, Zn, Pb; coloured glass – Cu, Pb, Cd**.**

## 3　Heavy metals at landfills

Due to the absence of industrial plants, many regions have landfills as main source of heavy metals. A lot of used things from residential and commercial sectors are transferred to landfills, where they can partly emit heavy metals compounds into the environment. Some part of heavy metals in waste at landfills is leached to the soil, which can accumulate a big amount of them. There is also a high heavy metals content in a landfill leachate, some metals are emitted into an air.

There is a high possibility for insoluble heavy metal compounds to react with other substances in or out of landfills and to form soluble compounds. Thus, such processes increase the concentration of soluble forms of heavy metals and raise environmental risks. The authors [36] have found Pb, Cd, Cr and Ni concentration in groundwater near the landfill lower the detection limit and have suggested these metals to be largely absorbed by soil.

To assess the pollution with heavy metals from landfills, the typical Ukrainian landfill (near regional centre Vinnytsia) was studied. Some heavy metals (Pb, Cd, Cr and Ni) concentration in the soil around the landfill (200 m distance) was determined using spectrophotometer with a fiery atomizer.

The results (see Table 1) did not show the excess of limit concentrations for any heavy metal. In majority of samples, the concentrations of Cr and Pb are near twice lower the permissible value, but are high enough to concern about (except samples 1, 2 and 3 for Cr and samples 3 and 4 for Pb). At the same time, Cd and Ni concentrations in all samples are significantly below their limits. Only samples 8 and 9 in the case of Cd and samples 1 and 4 in the case of Ni have relatively high content of these metals.

**Table 1.** Heavy metals concentrations in the soil near the landfill, mg/kg

| Metal | Limit | Samples | | | | | | | | |
|-------|-------|------|------|------|------|------|------|------|------|------|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Pb | 6 | 1.58 | 2.44 | 0.73 | 1.21 | 2.41 | 1.94 | 1.86 | 2.50 | 2.57 |
| Cr | 6 | 1.82 | 1.85 | 1.61 | 3.24 | 2.76 | 2.99 | 3.48 | 2.99 | 3.38 |
| Ni | 4 | 1.02 | 0.34 | 0.52 | 1.62 | 0.26 | 0.57 | 0.36 | 0.68 | 0.38 |
| Cd | 0.7 | 0.01 | 0.05 | 0.04 | 0.03 | 0.03 | 0.08 | 0.08 | 0.14 | 0.18 |

The heavy metals concentrations distribution was analyzed depending on the distance from the landfill. Cd content gradually decreases with increasing a distance to the landfill (except sample 4). Also, Cd concentration decreases towards the northeast, that corresponds to the location of sampling points (north-east from the landfill) and previous researches [4].

Spatial distribution of Cr concentrations is not evident. On the one hand, the concentrations of Cr in the samples 1, 6, 7 (far row from the landfill) are higher than in some neighbor points (samples 3, 4, 9). A similar result was obtained by [4], which has defined that Cr concentration in the soil at distances of 3-6 km from a landfill was higher in comparison to samples taken near the landfill. There was no any Cr concentration dependence on the distance from landfill in other research [36] as well. On the other hand, there are lower Cr concentrations in eastern part of the sampling area (samples 1, 2, 3), as well as for Cd. Therefore, we can assume relatively active Cr migration in the soil, and places with higher concentrations have better conditions for distribution. This assumption is confirmed in [38], that has concluded that significant portion of Cr at landfills exists in oxidized form. For the insoluble $Cr(OH)_3$ formation it is required a neutral or slightly alkaline environment. It is not usual for many landfills, where anaerobic phase and acidic environment last a long time due to high organic content. Another explanation for the uncertain distribution of Cr in the soil may be the low effect of the landfill on its concentration, so other sources of Cr have a stronger influence.

Western part of the sampling area has higher Pb concentrations in comparison to eastern part. Thus, the dynamics of Pb and Cr concentrations are similar. In the case of Pb, dynamic is less clear and there are several points which do not correspond to general trend. This may indicate little impact of landfill on Pb concentration in soil at the study area. For example, the authors [39] have investigated that 80% of Pb at landfills are

found in the form of insoluble carbonates. Thus, Pb compounds do not migrate intensively from landfills to soils.

Ni concentrations at investigated area don't have any evident spatial distribution. There is the research [37] where concentration of Ni in soil was investigated to be decreased sharply during the first 100 meters from a landfill, and then its concentration varied little. We can therefore assume that in our case, at a distance of 200 meters from the landfill, its impact on Ni concentration in soil is minimal.

There is the research [38] with heavy metals concentrations in soil at the area of landfills influence not exceeding the permissible values (sampling depths were 1-6 m). The concentration ranges of Pb, Cr, Ni, Cd were 0.2-1.6, 0.06-0.97, 0.06-0.44 and less than 0.2 mg/kg respectively. There are significantly higher Pb concentrations in our research, while Cr and Ni concentrations are only slightly higher. Other authors [4] have determined the total contents of heavy metals (Pb, Cr and Ni) in soil near landfill, which were 1.5-3 times higher in comparison to their background concentrations. Cr concentration ranged from 100 to 120 mg/kg, Ni – from 62 to 92 mg/kg, Pb – from 25 to 60 mg/kg. These data confirm that majority of the heavy metals considered exist in soils in bound form after migration from landfill.

Comparing the heavy metals concentrations in soils near the investigated landfill to those measured near other landfills, one should note much lower concentrations at the investigated territory. These results indicate strong negative consequences of the wrong landfill site selection and failure to comply with the rules of landfill construction and operation. In the case of developing countries, landfills do not meet with the environmental requirements and heavy metals concentrations in soils nearby are several times higher in comparison to those in soils near investigated landfill (there are also environmental problems, but this landfill meets the requirements much more).

Therefore, there is a potential risk of soil contamination by Cr and Pb (to a lesser extent) in the impact zone of investigated landfill, while the pollution levels of Cd and Ni are negligible. Also, despite the proximity of the sampling points to each other, one should note significant changes of the heavy metals concentrations, especially Pb and Ni.

## Prediction of heavy metals in the leachate

To simulate and predict natural degradation processes occurring in landfills, the landfill simulation reactors (LSR) were used. Authors [40-43] have already demonstrated the ability to reproduce long-term processes in landfills within a short period of time. The mixed waste was used for the experiment. 2 waste mixtures had a following content. Mixture 1: organic 30%, glass 20%, paper 10%, construction materials 9%, wood 8%, plastic 7%, hazardous waste 6%, rubber 3%, metals 3%, textile 1%, other 3%. Mixture 2: organic 48%, glass 8%, paper 10%, construction materials 6%, wood 6%, plastic 6%, hazardous waste 1%, rubber 2%, metals 2%, textile 6%, other 5%. The water content was determined for both mixtures (water contents: 33.51% – 41.29%). The difference in the water content is mainly due to the difference in the content of organic matter, which is the most water-containing fraction. Reactors were thermo-isolated and heated by a water cycle. An optimal temperature range for anaerobic microorganisms was 37 ºC. The LSR provide the possibility of continuous leachate circulation. To simulate landfill conditions and constant waste moistening each reactor was equipped with a pump connected to the bottom and the top of reactor. The duration of the research – 12 weeks. The leachate was sampled once a week and the same volume replaced by fresh water. The added water quantity corresponds to natural downfall on landfills (average 650 mm/y). The concentrations of four heavy metals (Pb, Cd, Ni, Cr) in the leachate were analysed by Atomic Absorption Spectrometer with Flame and Graphite Furnace. pH, reduction potential, electrical conductivity, dissolved organic carbon (DOC), and chemical oxygen demand (COD) were also measured.

The leachate pH after a dramatic rise at the beginning of the experiment (to almost neutral value in the reactor 2) then slowly decreased (to 5.3-5.6 at the end). This indicates that acidogenesis (accumulation of acids resulting from anaerobic fermentation processes in the waste body) continued during the whole period of the experiment and stabilization has not occurred. After the 5th week the leachate of the reactor 2 had only slightly higher pH while twice higher content of organic matter in comparison with that in the reactor 1. That allows suggesting small effect of waste composition on the leachate acidity at later stages. It is known that low pH corresponds to young landfills and provides a high solubility of many hazardous substances and their high concentration in a leachate.

The redox potential increased constantly except the first 5 weeks for the leachate of LSR2, when there was a significant decrease, which corresponds to the pH dynamics in this reactor. During the first 5 weeks there were significant differences between two reactors in the dynamics of pH and redox potential of the leachate.

Very low conductivity values at the beginning of the experiment are due to the low water content in the reactors for starting the active processes of substances leaching from the waste body. Slightly higher values of electrical conductivity in the leachate of the reactor 2 correspond to higher content of dissolved salts because of higher content of organic matter in the waste mixture in the reactor 2.

Dissolved organic carbon (DOC) has increased dramatically in both reactors during the first few weeks and then slowly decreased (one week later in the reactor 2). The early increasing can be explained by the fact that in 2nd week the fresh water was added to the LSR to intensify the leachate circulation. This caused the release of easy soluble organic components of the waste. Gradual reduction of organic carbon in the leachate is common for landfills and is associated with quick degradation of organic matter at waste body. Thus, after active phase the content of organic matter becomes lower in both waste body and leachate.

Chemical oxygen demand (COD) of the leachate had similar trend. The decrease of this parameter is more intensive than the decrease of DOC. Higher values of DOC and COD in the leachate of the reactor 2 are a consequence of higher content of organic matter in this reactor. The organic mass in LSR2 is almost 3 times higher than in LSR1, but the difference between the DOC values is only 1.5 times. Therefore, we can compare DOC and COD values per 1 kg of organic matter in both reactors. Calculation shows 1.5-2 times exceeding of DOC and COD values per 1 kg of organic matter in LSR1. This may indicate that the higher the easy degradable organic content, the less is relative rate of leaching of organic substances. This increases the time when a landfill poses a risk to the environment due to the presence of organic matter. High COD values at the end of the experiment (respectively about 40,000 and 66,000 mg/l for LSR1 and LSR2) indicate the active anaerobic phase and long-time dissolution of organic matter.

The main sources of heavy metals in the waste, therefore, were batteries (especially for Ni), plastic and rubber (especially for Cr). For the purpose of the investigation, we need to know how the heavy metals concentrations are varied over time in the reactors leachate. Results are shown in the Table 2.

Lead concentration in the leachate was very similar in both reactors, but clear dynamics over the time was not observed. Concentration of lead slowly began to decrease after the growth in the first 4 weeks (more drastic changes in the reactor 2, mostly due to differences between the reactors in pH and redox potential of the leachate at that time). It is usual process when substances leach from a waste more intensive at the beginning. When easy-soluble forms of Pb were leached quickly and intensity of this process became slower, then lead concentration in the leachate decreased as well. So, first half of the experiment has occurred in accordance to usual chemical processes in waste body. After reaching a minimum at 8th week, Pb concentration rapidly increased to maximum value (about 1 mg/l). This is perhaps due to non-uniformity of processes inside the reactor, because any drastic changes of other parameters did not happen at 8th week. Lead concentration slowly decreased during last weeks but still was high (more than 0.5 mg/l). This allows to suppose that perhaps liquid streams achieved some source of lead inside reactors at 8th week and this source sent a lot of lead substances to the leachate. Such processes are likely to occur at landfills as well. They are more evident and more noticeable in landfill simulation reactors due to their small scale. Pb content corresponds to its average values in the leachate of old landfills of Ukraine or other countries with similar morphological composition of waste [36]. But these values are significantly higher than those which one can find in the studies that use landfill simulation reactors: the authors [42, 44] report about maximum Pb concentrations in the leachate less than 0.2 mg/l. That is because concentration of heavy metals in a leachate depends on the its content in the input material.

**Table 2.** Heavy metals concentration in the leachate samples, mg/l

| week | Cd | | Cr | | Pb | | Ni | |
|---|---|---|---|---|---|---|---|---|
| | LSR1 | LSR2 | LSR1 | LSR2 | LSR1 | LSR2 | LSR1 | LSR2 |
| 2 | 0.001 | 0.004 | 0.035 | 0.046 | 0.009 | 0.015 | 0.74 | 3.31 |
| 3 | 0.001 | 0.009 | 7.275 | 34.78 | 0.044 | 0.508 | 0.87 | 2.84 |
| 4 | 0.0005 | 0.005 | 2.3 | 18.541 | 0.154 | 0.502 | 0.88 | 3.24 |
| 5 | 0.0006 | 0.001 | 1.543 | 4.63 | 0.075 | 0.12 | 0.9 | 2.66 |
| 6 | 0.0007 | 0.0009 | 1.145 | 3.115 | 0.119 | 0.106 | 0.97 | 2.39 |
| 7 | 0.0005 | 0.001 | 1.308 | 2.483 | 0.013 | 0.019 | 0.99 | 2.1 |
| 8 | 1.929 | 1.963 | 1.209 | 2.808 | 0.783 | 0.879 | 1.06 | 2 |
| 9 | 1.924 | 2.063 | 1.009 | 2.544 | 0.561 | 0.9 | 0.96 | 2.19 |
| 10 | 1.805 | 1.867 | 0.932 | 2.718 | 0.704 | 0.895 | 0.96 | 2.37 |
| 11 | 1.845 | 1.858 | 0.927 | 2.088 | 0.776 | 0.757 | 1.06 | 1.89 |
| 12 | 1.833 | 1.913 | 0.843 | 1.845 | 0.536 | 0.688 | 0.89 | 2.26 |

Both reactors have significantly different nickel concentration dynamics. The concentration in the leachate of LSR2 was 2-3 times higher and tended to decrease, while Ni concentration in the leachate of LSR1 slowly increased. All other leachate parameters of both reactors have similar dynamics. Therefore, dynamics of Ni concentration in LSR2 leachate corresponds to natural processes in waste body at landfills. Instead, there is a stable increasing of Ni leaching in LSR1. The causes of such leaching have to be batteries presence and constantly low pH. In general, the values of Ni concentration correspond to its content in the leachate of old landfills (0.4-3 mg/l) and to the results obtained by previous researchers [44, 45]. They have investigated that solubility and mobility of heavy metals in landfills can be increased by active decomposition of organic matter due to the formation of soluble complexes of high acids with heavy metals (e.g., amino acids). We can therefore conclude that high content of organic matter helps to increase the leaching of heavy metals from a landfill body. On the example of nickel, it is clearly seen that much higher content of organic matter in the reactor 2 causes also significantly higher Ni concentrations in its leachate despite of higher pH values. This can be explained by active formation of soluble Ni-organic complexes.

The chromium concentration in the leachate of both reactors dramatically increased during the first 3 weeks. The concentration has immediately decreased to 1-1.5 mg/l just after that and then gradually decreased. It corresponds to typical behavior of contaminants as mentioned above. A similar dramatic increase of the concentration during this period is noted for the lead. The value of electrical conductivity also dramatically increased on the 3rd week because one week before the fresh water has been added to the reactors to intensify the leachate recirculation, which led to quick leaching of substances from the waste body. Such dynamics is also proved by other studies. Much more intensive jump of Cr concentration in the leachate of LSR2 in comparison to LSR1 can be explained by dramatic increase of leachate pH in LSR1. This has smoothed the rise of Cr concentration resulting from adding the fresh water. In the same time pH in LSR2 was still low in first weeks. It has allowed active chromium compounds leaching which was the most significant among heavy metals studied. Therefore, we can consider chromium as most accessible for intensive leaching from a waste body. Also, the concentration of Cr in the leachate of LSR2 was higher compared to the leachate of LSR1. It should be noted that fluctuations of the Cr content correspond to the changes that occur with the physico-chemical parameters of the leachate (dramatic jumps on 2nd-4th weeks followed by stabilization). Besides, relatively low Cr concentration in leachate after the 4th week (1–4 mg/l) is too high in comparison to results obtained by other authors [41,43]: less than 1 mg/l) for more or less similar waste composition. But they are relevant for Ukrainian landfills leachate as reported in [42].

Cadmium content in the leachate of both reactors varied in different ways during the first half of the experiment. In the leachate of LSR1 the concentration slowly decreased, and in the leachate of LSR2 there was a surge of concentration on the 3rd week (from 3.92 to 9.32 mg/l) and the same drastic reduction in next 2 weeks (from 9.32 to 1.13 mg/l). Such dynamics is also the same for Cr and Pb. After the 5th week Cd concentration in both leachates were similar with the low prevalence in the leachate of LSR 2. There was a dramatic increase of the concentration of Cd on the 8th week in both reactors as it was in the case of Pb. This fact needs to be focused on. It seems to be similar to increase the concentrations of Ni and Cr on the 3rd week. The 3rd week is really characterized by significant changes in the conditions inside the reactors. The 8th week is not especial one, there were no any big changes of physico-chemical parameters. So, most likely that since the 8th week water flows inside the reactors came to places of accumulation of Pb and Cd, since different types of waste contain different quantity of metals, and even waste mixing does not provide uniform distribution of substances in the waste mass. This is especially adjusted for Cd, since 99% of it comes to waste with batteries. The increase of Cd concentration in the leachate was the most dramatic after the 8th week. Similarly, one can explain the significant excess of Ni concentration in the leachate of the LSR2 since Ni comes to waste mainly with batteries as well. Thus, great variety of Cd concentration in both reactors relate very well to the idea about presence of only one powerful source of cadmium with small spatial dimensions disseminated over the waste body. We can conclude that this fact has a big role taking into account small size of reactors in compare to natural landfills.

The low pH has resulted in high content of heavy metals in the leachate because it is easier for metals to dissolve and wash out in acidic environment [43]. There are peak concentrations of Cr, Pb and Cd in the leachate of LSR2 on the 3rd week, which is the result of dissolution due to adding fresh water and increasing the amount of circulating leachate. As a result, majority of dissolved compounds of the heavy metals were leached on the 3rd week. At this time the leachate of the reactor 2 had pH lower than that in the reactor 1 (4.7 and 5.55 respectively). This has created conditions for intensive transformation of Cr, Pb and Cd compounds in soluble form and intense leaching, while the pH in the reactor 1 (5.55) was enough to dissolve these compounds relatively slowly. The absence of such changes of Ni concentration can be explained by less impact of pH in these conditions and greater role of other factors such as the formation of soluble organic complexes mentioned above. In overall, results show that pH can influence on heavy metals concentration in leachate more significantly than heavy metals content in input waste.

To predict the rate of acceleration of the processes that take place in the LSR, we should compare the water balance in LSR and in a real landfill. The water-solid ratio is determined as water volume (passed through a waste body) divided on waste mass. Taking into account the well-known statistics, waste masses in LSR1 and LSR2 (33 kg and 40 kg respectively), and water volumes added during the experiment (64.3 l and 68.3 l respectively), we can define water-solid ratios for the reactors: LSR1 – 1.948 l/kg*year, LSR2 – 1.708 l/kg*year. Comparing the water balance, we can calculate the acceleration factors for both reactors: LSR1 – 244, LSR2 – 214. It means that 12-week experiment has reproduced 56 and 49 years of the landfill lifetime in the reactors 1 and 2 respectively. The results show that biological processes do not end even after half-century, and the concentration of heavy metals in the leachate is still very high. There is no concentration of any heavy metal lower than allowable values even after 50-60 years. For example, the Pb content at the end of this period is 5-6 times higher than the permitted value (0.01 mg/l), Ni – 2-4 times (0.5 mg/l is allowed), Cr − 8-18 times (0.1 mg/l is allowed). The most catastrophic situation is for Cd − 180 times excess (0.01 mg/l is allowed). According to [41], high COD values (up to 90000 mg/l) are typical for young landfills. Therefore, COD concentrations, obtained at the final stage of the experiment, meet young-age landfill. For example, the leachate of 20-30 years old landfills has the average COD level 1600 mg/l. This relatively slow evolution of processes in the LSR can be caused also by high content of heavy metals. In [41], the author has studied that concentration of heavy metals in the leachate more than 1 mg/l can be toxic and stops biochemical processes of waste decomposition.

## 4    Conclusion

Household waste and landfills, where they are accumulated, have become a powerful source of heavy metals in recent years. The analysis of the sources of heavy metals delivered into the environment together with waste shows the large scale of predictable pollution. A lot of different fields of human activity supply heavy metals to the environment. First of all, these are electrical appliances, batteries and accumulators, sewage sludge, ash and slag of waste incineration plants, and waste pesticides and fertilizers. There are not only inert compounds delivered into the soils and water bodies, but also a large amount of mobile (available) form of metals. Under certain conditions they are able to change the environment significantly.

The analysis of concentrations of heavy metal mobile forms in soil near landfills shows that allowable limits are not exceeded. Besides, the heavy metals concentrations in soil at the study area are lower compared to those in soils near other landfills. This confirms that the wrong site selection and failure to comply with the requirements of landfill construction and operation have a significant impact on the soil contamination with heavy metals. Comparing obtained results with results of other authors, we can conclude that mobile forms of heavy metals present only a small part of their total content in soils near landfills. These are mobile forms which most likely come to the soil from landfill.

The experiment with landfill-simulating reactors was characterized by the acid phase, which is confirmed by the values of physico-chemical parameters. Especially pH indicates the long-time aggressive environment that certainly affects the leachate composition. The analysis of heavy metals concentrations shows their quite high level. The results show that the physico-chemical conditions inside the reactors have the largest impact on early stages, although there is noticeable effect of other factors in the case of Ni. However, there are also some exceptions, which are probably related to the unequal distribution of substances in the waste body (examples of Cd and Pb). The results also show that pH can influence on heavy metals concentration in leachate more significantly than heavy metals content in input waste. Transferring the results of landfill simulation reactors to real landfills shows a significant excess of permissible concentrations of heavy metals in the leachate even after dozens of years of waste accumulation. This is of serious concern and should be taken into account in the case of further landfills operating.

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