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Technogenic impact of acid tar storage ponds on the environment: a case study from Lviv, Ukraine

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Abstract. WA number of countries keep acid tar in the open air in spent quarries, barns, storage ponds (USA, UK, Netherlands, Belgium, Germany, Latvia, Slovenia, China) or near landfills (Zimbabwe). Storage of acid tars in open areas leads to an increase in regional environmental hazards. In Ukraine, acid tars are also stored in open spaces in storage ponds, in particular, in the city of Lviv near the municipal landfill. After the Lviv experimental petroleum-refining plant began to dispose of oil-refining waste at the Lviv city landfill, two ponds of acid tars were formed. Their total area is 6.8 ha. They were formed by constructing dams in the upper reaches of deep ravines, originating near the landfill. In total, about 300 thousand tons of acid tars have been accumulated in these earth basins. In 2004, the dams of the acid tar storage ponds got cracked. As a result, acidic water flows to the soil surface 1 km southwest of these storage ponds. Sampling for the study of acid tar migration was carried out from 4 sites of anthropogenic origin: 1 - acid tar storage pond No.1; 2 - acid tar storage pond No.2; 3 - technogenic water body at the foot of the landfill containing leacheate; 4 - technogenic water body on the north side of the landfill containing leacheate. The simulation was made by Surfer software. It was found that even after many years of their creation, a very high content of sulfuric acid is observed in the ponds (1,108-3,862 mg / kg), and they remain a major environmental hazard. The simulation results made it possible to assess the migration of toxic components contained in the tar to the components of the biosphere - the hydrosphere and ecotope. It was established that, unlike other investigated technogenic water bodies, acid tars in the storage ponds have high content of petroleum products, sulphates, phosphates, suspended substances, and high rates of chemical oxygen demand. The high content of petroleum products suggests that acidic tars can be processed into liquid fuel by freeing them from excess water and salts. At the same time, these large quantities of petroleum products pose an environmental threat to soil and groundwater, thereby reducing regional environmental security.

Key words: acid tar, civil protection, petroleum products, environment, landfill.

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Introduction

A number of countries keep acid tar in the open air in spent quarries, barns, and storage ponds (USA, UK, Netherlands, Belgium, Germany, Latvia, Slovenia, China) or near landfills (Zimbabwe, Ukraine). Storage of acid tars in open areas leads to an increase in regional environmental hazards (Popovych et al., 2018). Any storage of industrial waste has a detrimental effect on living organisms (Popovych et al., 2018; Kuzmenko et al., 2018). Many international research papers are devoted to this topic.

In particular, an analysis of the content of the main pollutants in the aqueous phase of a quarry with acid tar (petroleum products and sulphates) showed a strong pollution with petroleum products. The fluorimetric method revealed a vertical gradient of petroleum product content in depth - from 6.4 mg / dm^3 in surface to 1,995 mg / dm^3 in the depth of 1 meter in the bottom layers. The petroleum product content with depth increases by 312 times and significantly exceeds the maximum permitable concentration for water bodies (0.3 mg / dm^3) (Shilova et al., 2017). Soil samples were taken in the area near a quarry with acid tar, at a distance of 35-40 m and 150 m (at the border of the recreation area), taking into account the wind rose. Their analysis showed that with distance from the quarry the soil acidity decreased from pH 2.8 to pH 4.3. At a distance of 150 m, the acidity corresponded to the pH of brown forest soils (Shilova et al., 2017).

To date, dozens of copyright certificates and patents for acid tar processing have been received in the world. Most methods of disposal come to the regeneration of sulfuric acid from wastes or burning of neutralized tars. In Germany and the Netherlands, for example, waste is incinerated in enclosed boxes, while combustion products are not released into the environment (Popovich, 2016).

There are various ways of processing acid tars in the product that is not used, many scientists are trying to reduce the environmental problems, linking with recycling them in the lagoons (Družina, 2010). Some of the recycling processes considered included, among other things, the conversion of acid tars into asphaltenes, the production of pavement binders, energy generation. To reduce the negative impact on the environment, membrane technologies, ion exchangers and carbon adsorbents are used. However, these methods have not been fully investigated due to the complexity of acid tar structure. Accordingly, there remains a deep need for environmental stability (Danha et al., 2014).

Numerous studies have found that the addition of 10% additives by the total weight is sufficient to neutralize the free acids contained in acid tars. The resulting product is suitable for processing into bituminous mastic (Zharinov, 2015).

The work (Nadirov et al., 2019) presents the results of a study of the influence of technological factors on the saponification of fatty acids in cotton tars which are necessary for the development of a technology for the synthesis of new surfactants used in oil dehydration processes. Based on the data obtained, it was concluded that the effective concentration of alkali solution corresponds to 8-15%, while the amount of excess alkali does not affect the time of effervescence. Determined is the influence of temperature on the duration of the neutralization process. It was shown that fatty acids are a valuable and fairly affordable raw material used in various fields of the oil and gas industry; therefore, their extraction from waste, namely, from cotton tar, with their content of up to 65%, is appropriate and economically feasible.

In Ukraine, acid tars are stored in the open air in storage ponds, in particular in the city of Lviv near the municipal landfill. After the Lviv experimental petroleum processing plant began to discharge waste from the oil refining process at the Lviv city landfill, two ponds of acid tars were formed, which are still not managed in accordance with the requirements of the technological process (Popovych et al., 2015). It should be noted that in addition to storing garbage and acid tars, leacheates are released from deep within the landfill, which cause an additional technogenic load on the adjacent territory (Malovanyy et al., 2018; 2019; Popovych et al., 2015).

There are 2 acid tar storage ponds are in the landfill area. Their total area is 6.8 ha. They are formed by constructing dams in the upper reaches of deep ravines, originating near the landfill. In total, about 300 thousand tons of acid tars have been accumulated in these earth basins. In 2004, the dams of the acid tar storage ponds got cracked. As a result, acidic water flows to the soil surface of 1 km^2 southwest of these storage ponds (Khromyak et al., 2016).

The chemical composition of these tars in different years was studied by different organizations. Some of the most recent data (Khromyak et al., 2016) concerning the composition of acid tars are shown in Table 1.

In the zone of influence of the acid tar storage ponds, the soil, in terms of copper content, is the most polluted. In almost all samples, an excess of the MPC was recorded (Prykhodko, 2013). The minimum excess is 1.6, the maximum is 41.3 times. Nickel pollution is similar. However, both the average and maximum levels of soil contamination by these elements are significantly lower as compared to cadmium.

In some samples, the excess of MPC for zinc is recorded. For example, it reaches 9.5 times between the landfill and the dam of the tar pond. Soil contamination with chromium was detected in only two samples. The maximum excess reaches 1.7 times.

The content of cobalt and manganese in the soils does not exceed the MPC in any sample.

Particular attention is paid to soil contamination by leakage of acid tars which is traced in ravines south of the Lviv municipal landfill. The area of contamination only within one leakage exceeds 1 ha. No less large-scale leakages are recorded in another ravine, where the liquid phase of the tar forms a continuous flow. Slightly smaller leakage areas were discovered in the ravine at the top of which two acid tar ponds were created.

According to the analyses performed by the Ecology and Natural Resources Management Laboratory, the soils here have an acid reaction (pH 3.3–3.8), as well as an excess of MPC in lead by 34.2, copper - by 33, nickel - by 2.7, petroleum products - by 2 times (Leonard et al., 2010).

The object of the studies is acid tars which are stored in the open air. The subject of the studies is the hazardous components of acid tars and their migration into the biosphere. The purpose of work is to study physical and chemical properties of acid tars in the territory of a separate polygon to assess their technogenic threat to the environment.

Material and Methods

The following research methods were used in the work: methods of quantitative and qualitative analysis, of soil science, methods of chemical, physical, mathematical-statistical and system analysis.

Sampling for the study of acid tar migration was carried out from 4 sites of anthropogenic origin in the center of the pond from one spot (volume - 1.5 l). Sampling was carried out during July, 2019. Figure 1: 1 - acid tar storage pond No.1; 2 – storage pond of acid tars No. 2; 3 - technogenic basin at the foot of the landfill with the content of leacheates; 4 - technogenic basin on the north side of the landfill with the content of leacheates.

The samples were taken according to the recommendations given in the CPI 211.1.0.009-94. *Hydrosphere. Sampling to determine the composition and properties of wastewater and process water.* In the selected samples the following set of indicators (parameters) was determined:

Organoleptic:

- colour, transparency, odor - according to the reference book by Lurie (1984).

Physical:

- suspended substances, dry residue, mineral residue - by gravimetric methods (measuring instruments - analytical scales, laboratory thermometers).

Physico-chemical:

•pH value, total mineralization - by potentiometric methods in accordance with the instructions for the respective devices (devices - a pH-150I pH meter, a TDS universal salimeter).

Chemical:

•total hardness, alkalinity (carbonate hardness), content of carbohydrates by titrimetric methods with trilon B and hydrochloric acid;

• chloride content - by titrimetric method with silver nitrate;

• sulphate content - by gravimetric method (instrument - analytical balance);

• nitrite content – by photometric method with Griss reagent (device –a KFK-2 electro-photocolorimeter);

•nitrate content - by photometric method with Griss salicylic acid (device – a KFK-2 electro-photocolorimeter);

•ammonium ion content - by photometric method with Nesler Griss reagent (device – a KFK-2 electro-photocolorimeter);

•phosphate content - by photometric method with the combined *molybdenum reagent* and ascorbic acid (device – a KFK-2 electro-photocolorimeter);

•iron content – by photometric method with rhodanide (device – a KFK-2 electro-photocolorimeter);

•chemical oxygen demand (COD) - by titrimetric method with potassium dichromate;

•petroleum products content - by gravimetric method with chloroform and hexane (instrument - analytical balance).

Results and Discussion

The results of studies on the physicochemical parameters and chemical composition of acid tar samples from the storage ponds are presented in Table. 2.

As can be seen from Table 2, even after many years since the filling of tar ponds, their acidity is significant (pH < 3). This means that the content of acids (in particular, sulfuric acid) in the tars studied is very high. It is many times higher than the MPC for wastewater and constitutes a significant environmental hazard for both the soils surrounding the ponds and groundwater in the vicinity of the landfill. By the high solids content it can be judged that these tars contain a huge amount of salts. Moreover, the bulk of these salts are mineral salts, as evidenced by the ratio of dry residue (dried at + 90 ° C) and mineral (calcinated at + 800 ° C).

Table 1. Composition of tars stored at the Lviv city landfill (Khromyak et al., 2016).

Component	Content by weight,%
Carbohydrates	20.6
Resins, carbon, carboids, ash, oxidation products	78.2
Sulphuric acid and sulfonic acids	1.2
Acid number (mg KOH / g)	14

Fig. 1. Indicative map of the research areas.

Table 2. Physico-chemical properties of the samples.

No.	Indicator	Measurement units	Sample 1	Sample 2	Sample 3	Sample 4
1.	Odor at 20 ° C	points	1.5	1.5	2	1.5
2.	pH value	pH unit	2.2	2	8.1	2.1
3.	Suspended substances	mg/dm^3	154	198	46.2	54.8
4.	Dry residue (+90 °C)	mg/dm^3	7.248	6.857	11.554	7.130
5.	Mineral residue (+800 °C)	mg/dm^3	6.306	5.947	7.320	6.180
6.	Total hardness	$mg\text{-}equi/dm^3$	57.4	62.3	26.4	82
7.	Chlorides (Cl^-)	mg/dm^3	794	712	2.045	774
8.	Sulphates (SO_4^{2-})	mg/dm^3	3.625	3.862	1.108	3.716
9.	Nitrates (NO_3^-)	mg/dm^3	94.3	85.4	158.3	86.3
10.	Phosphates (PO_4^{3-})	mg/dm^3	12.7	9.5	12.8	3.6
11.	Ammonium salts (NH_4^+)	mg/dm^3	39.2	36.5	92.3	56.2
12.	Total iron (Fe_{total})	mg/dm^3	14.6	12.1	68.2	56.3
13.	The sum of (Na^+) + (K^+).	mg/dm^3	408	387	2.203	400
14.	Chemical oxygen demand (COD)	mgO/dm^3	332	491	265	132
15.	Petroleum products	mg/dm^3	523	488	1.69	23.6

The spatial distribution of odor (in points), pH, suspended substances, dry and mineral residues, and total hardness in the technogenic water bodies of the Lviv city landfill are shown in Fig. 2.

The difference between dry and mineral residues correlates well with the numerical values of petroleum product content and COD. That is, at + 800 ° C, it is the organic components of tars that burn out - petroleum products, organic acids and their salts. The same indicators (high content of petroleum products) suggest that these tars can be processed into liquid fuel by freeing them from excess water and salts. At the same time, these petroleum products in large quantities pose an environmental threat to soils and groundwater (as does sulfuric acid). The spatial distribution of petroleum products, COD and the amount of (Na^+) + (K^+) in technogenic basins of the Lviv city landfill is shown in Fig 3.

Very high sulphate content in the samples confirms the assumption of a significant amount of free sulfuric acid in the tar.

The complete absence of nitrites in the studied samples and the relatively low content of ammonium in them indicate aggressive oxidative conditions in these ponds, which excludes the existence of any living microorganisms in them. For the same reason, the leakage of these tars through the protective dams or soil banks can be a deadly threat to the plants and animals in the vicinity of the storage ponds. The spatial distribution of chlorides, sulphates, nitrates, phosphates, ammonium salts, and total iron is shown in Fig 4.

Table 3 presents values showing the multiplicity factors of exceeding the actual values of certain parameters determined in the investigated samples of acid tars, relative to the MPC for wastewater.

In fact, our studies confirm the data (Leonard et al., 2010) on the hazard of acid tars for the environment. Researchers found (Leonard et al., 2010) that the studied samples of acid tars contained aliphatic carbohydrates, cyclic carbohydrates, up to 12 primary polycyclic aromatic carbohydrates and many other organic groups, including organic acids (sulfonic acids, carboxylic acids and aromatic acids) phenyl, nitrile, amide, furan, thiophene, pyrrole and phthalates, many of which are toxic. An analysis of metals shows that Pb was present in significant concentration. The results show different transition peaks of the tested samples, which indicates their complexity and variability. The analysis further confirmed the presence of organic groups identified by GC/MS.

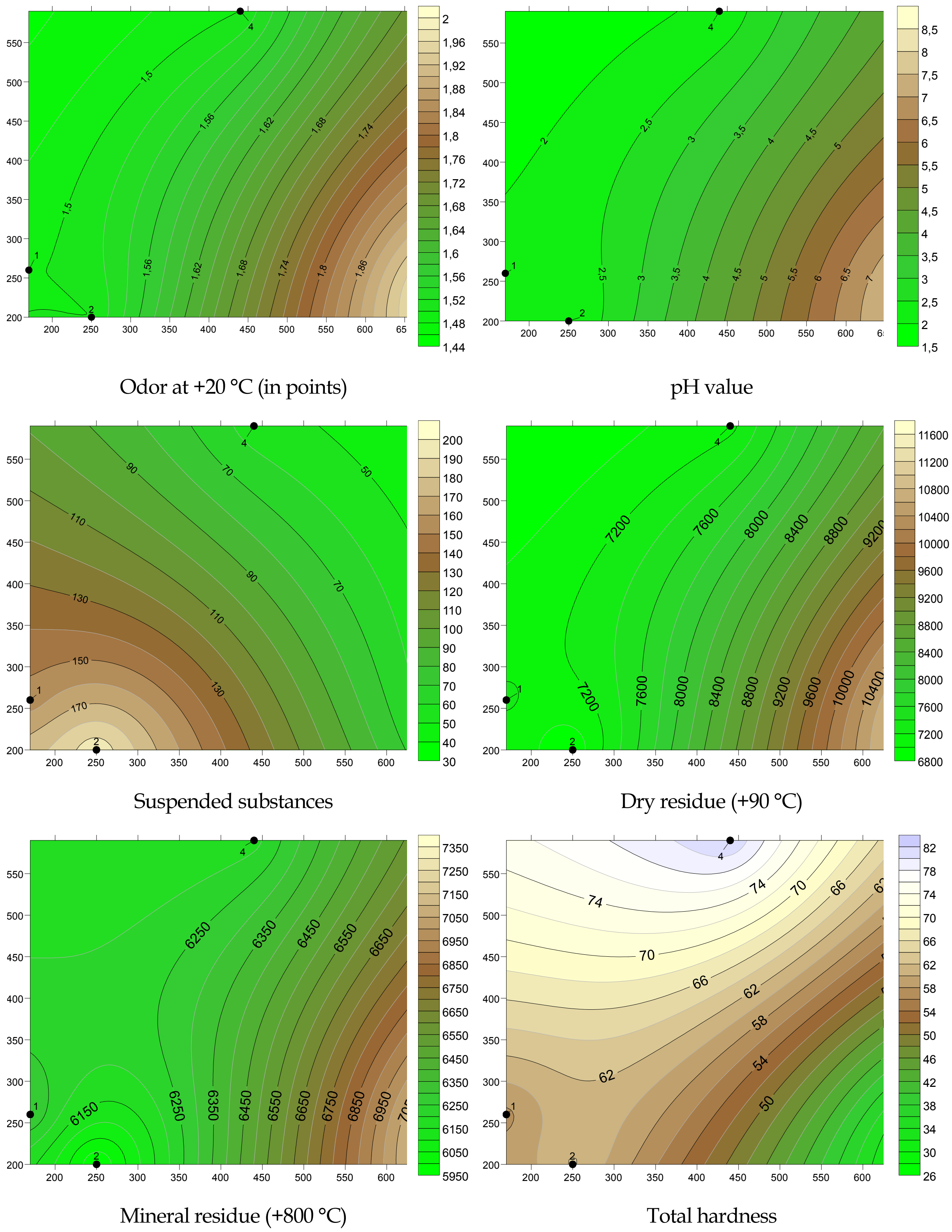


Fig. 2. The spatial distribution of odor (in points), pH, suspended substances, dry and mineral residues, and total hardness in the technogenic water bodiesof the Lviv city landfill.

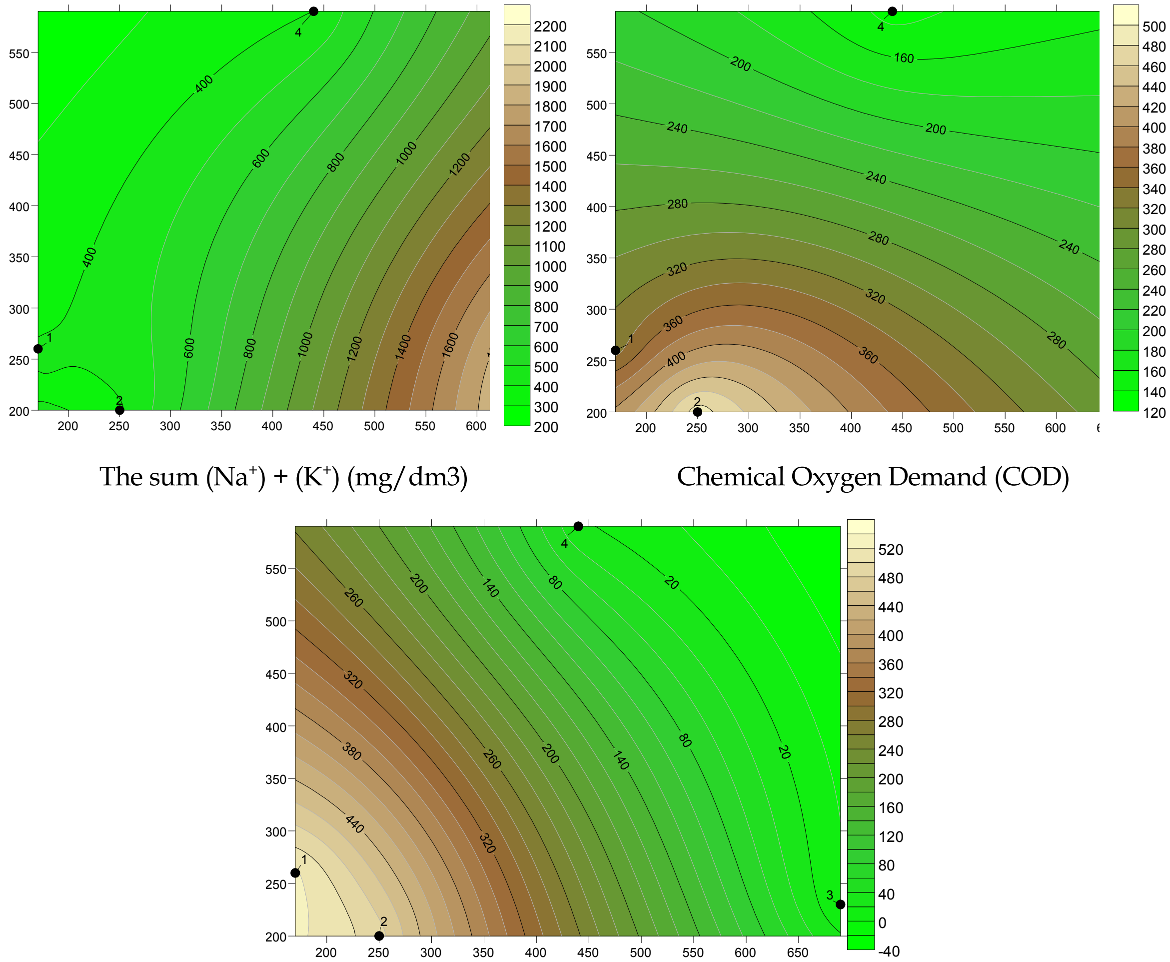
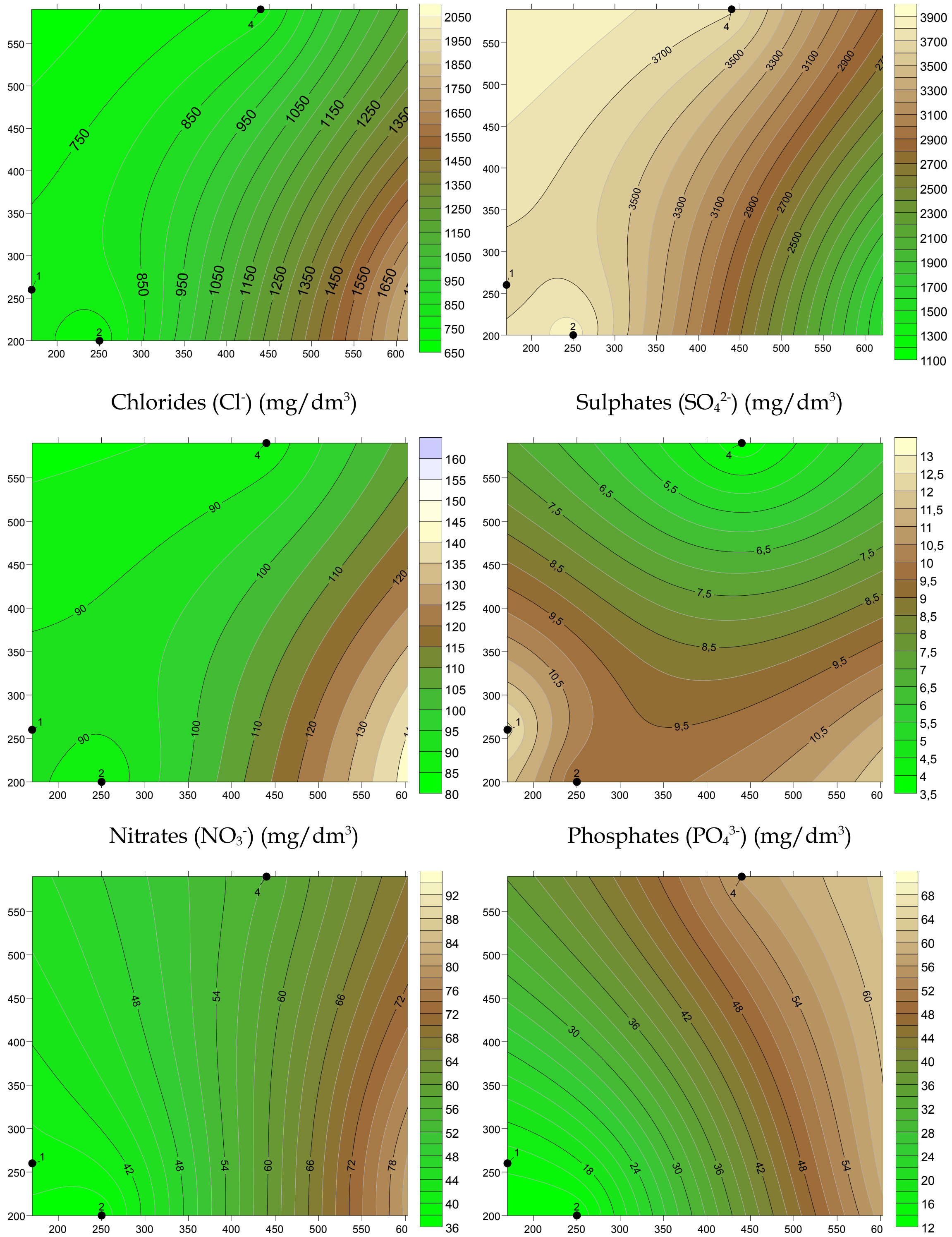


Fig. 3. Spatial distribution of petroleum products, COD and the amount of $(Na^+) + (K^+)$ in technogenic basins of the Lviv city landfill.

Table 3. Physico-chemical properties of the samples.

Item No.	Indicator	Measurement units	MPC	MPC excess	
				Sample 1	Sample 2
1.	Dry residue (+90 °C)	mg/dm^3	1,000	7.25	6.86
2.	Chlorides (Cl^-)	mg/dm^3	350	2.27	2.03
3.	Sulphates (SO_4^{2-})	mg/dm^3	500	7.25	7.72
4.	Nitrates(NO_3^-)	mg/dm^3	45	2.10	1.90
5.	Ammonium salts (NH_4^+)	mg/dm^3	38	1.03	0.96
6.	Total iron (Fe_{total})	mg/dm^3	2,5	5.84	4.84
7.	Chemical Oxygen Demand (COD)	mgO/dm^3	810	0.41	0.61
8.	Petroleum products	mg/dm^3	10	52.30	48.80



Chlorides (Cl^-) (mg/dm^3) | Sulphates (SO_4^{2-}) (mg/dm^3)

Nitrates (NO_3^-) (mg/dm^3) | Phosphates (PO_4^{3-}) (mg/dm^3)

Ammonium salts (NH_4^+) (mg/dm^3) | Total iron (Fe_{total}) (mg/dm^3)

Fig. 4. Spatial distribution of chlorides, sulphates, nitrates, phosphates, ammonium salts, and total iron

The results of micromechanical analysis made it possible to understand the surface characteristics of the samples and show that the distribution of pollutants is heterogeneous. The results obtained (Leonard et al., 2010) provide useful data on the composition, complexity and variability of acid tars, information on which is limited.

It was found that the most threatening pollution factor for territories adjacent to the acid tar storage ponds are petroleum products, sulphates and total iron content.

One of the most effective methods for cleaning soil contaminated with acid tars is phytomelioration (Popovich, 2016). In particular, in (Edenborn et al., 2015) the bio-coal from hard wood was studied for its potential use in phytostabilization of heavily contaminated soil in the territory of a sulfuric acid processing plant. The soil, which remained uninhabited for almost a century, contained a high concentration of lead, arsenic and antimony, and was both highly acidic and hydrophobic due to the presence of oil-based acid tar. Three approaches to application were tested with 10 and 20% (volume / volume) bio-coal: incorporation into the soil, top dressing on the surface, and layering in the soil. It was found (Edenborn et al., 2015) that uniform mixing of bio-coal from hard wood into the soil will facilitate rapid restoration in this area due to its low alkalinity with respect to the very high acidity of the existing soil. The surface application of bio-coal led to the most successful growth of *Elymus canadensis*.

Conclusions

Physicochemical analysis of acid tar samples from 2 storage ponds showed that even many years after their creation, a very high content of sulfuric acid in them remains a major environmental hazard. The simulation results made it possible to estimate the migration of toxic components contained in the tar into the biosphere components - hydrosphere and ecotope. It was found that, unlike other investigated technogenic water bodies, acid tars in the storage ponds have high indexes of petroleum products, chemical oxygen demand, sulphates, phosphates, and suspended substances.

The content of acids (in particular, sulfate acid) in the investigated acid tars is very high. It is many times higher than the MPC for wastewater and constitutes a significant environmental hazard for both the soils surrounding the ponds and groundwater in the vicinity of the landfill. The high sulfate content in the samples confirms the assumption of a significant amount of free sulfuric acid in the tars. The high content of petroleum products makes it possible to state that acid tar can be processed into liquid fuel by freeing it from excess water and salts. At the same time, these petroleum products in large quantities pose an environmental threat to soils and groundwater.

References

Danha, C., Chihobo, C., Musademba, D., Simbi, D., Kuipa, P. & Jonathan, E. (2014). Characterization and utilization of acid tar waste from crude benzol processing for environmental sustainability. *Journal Of Environmental Science, Toxicology And Food Technology, 8* (1, III), 16-21. doi: 10.9790/2402-08131621.

Družina, B. & Perc A. (2010). Remediation of Acid Tar Lagoon. *Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy*, 15, Article 17, (pp. 195-209).

Edenborn, S., Edenborn, H., Krynock, R. & Haug, K. L. (2015). Influence of biochar application methods on the phytostabilization of a hydrophobic soil contaminated with lead and acid tar. *Journal of Environmental Management*. 150. 226-234. doi: 10.1016/j.jenvman.2014.11.023.

Ganin, E., Dautov, R., & Ivanova, Y. (2017). Topical directions of waste processing of oil refining enterprises (acid tar). *In Eurasia Science: Collection of Articles VII of the International Scientific and Practical Conference,* (pp. 164-166) (In Russian).

Khromyak, U. & Tarnavsky, A. (2016). The impact of the *Zbyranka* LUE on the environment and the basic principles of creation of a new landfill. *Scientific Bulletin of UNFU*, 26.05, (pp. 227 – 232). (In Ukrainian).

Leonard, S., Stegemann, J. & Roy, A. (2010). Characterization of acid tars. *Journal of Hazardous Materials.* 175: 382–392. doi: 10.1016/j.jhazmat.2009.10.015.

Lurie, Y. (1984). Analytical chemistry of industrial wastewater. Moscow, USSR: Khimiya. (In Russian).

Malovanyy, M., Moroz, O., Hnatush, S., Maslovska, O., Zhuk, V., Petrushka, I., Nykyforov V. & Sereda A. (2019). Perspective technologies of the treatment of the wastewaters with high content of organic pollutants and ammoniacal nitrogen. *Journal of Ecological Engineering*, *20(2),* 8–15. doi: 10.12911/22998993/94917.

Malovanyy, M., Zhuk, V., Sliusar, V. & Sereda, A. (2018). Two stage treatment of solid waste leachates in aerated lagoons and at municipal wastewater treatment plants. *Eastern-European Journal of Enterprise Technologies, 1*(10), 23-30. doi: 10.15587/1729-4061.2018.122425.

Nadirov, K., Otarbaev, N. Sh., Nadirov, R., Kapustin, V., Sadyrbaeva, A. & Bimbetova, G. Zh. (2019). Separation of free fatty acids from cotton tar. *News of the Academy of Sciences of the Republic of Kazakhstan. Series of Geology and Technical Sciences, 4*, 70-78. doi: 10.32014/2019.2518-170X.99.

Popovich, V. (2016). Phytomeliorative recovery in reduction of multi-element anomalies' influence of devastated landscapes. *Biological Bulletin of Bogdan Chmelnitskiy Melitopol State Pedagogical University, 6(1)*, 94-114. doi: 10.15421/201606.

Popovych, V. & Kucheryavyi, V. (2015). Ecological danger of leacheate water bodies of landfills. *Collection of scientific works Visnyk of LDUBZHD, 12,* (pp. 77-84). (In Ukrainian).

Popovych, V., Stepova, K., & Prydatko, O. (2018). Environmental hazard of Novoyavorivsk municipal landfill. *MATEC Web of Conferences 247, 00025.* doi: 10.1051/matecconf/201824700025.

Popovych, V., Kuzmenko, O., Voloshchyshyn, A. & Petlovanyi, M. (2018). Influence of man-made edaphotopes of the spoil heap on biota. *E3S Web of Conferences*. *Vol. 60. 00010.* doi: 10.1051/e3sconf/20186000010.

Prykhodko, M. (2013). Ecological safety of natural and anthropogenically modified geosystems. Monograph. *Center for Environmental Education and Information.* 201 p. (In Ukrainian).

Shilova, A., & Gladun, I. (2017). The impact of acid tar quarry on the environment. *Science today: Fundamental and applied research: Proceedings of the international scientific-practical conference*, (pp. 126-127). (In Russian).

Zharinov, I. (2015). Neutralization of acid tars. *International journal of applied and fundamental research*, *12-10,* 1756-1758. (In Russian).

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