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The rationale for the recovery of the territories contaminated by organomineral waste

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Abstract. The article presents the results of surveys conducted on three areas contaminated with organomineral and petroleum-containing waste. The selected research sites included a location affected by a fuel oil spill, a geoenvironment contaminated with petroleum products, and a territory of unauthorized disposal of distillery waste. Comprehensive engineering surveys were carried out on all sites, with some of them including engineering-geophysical surveys. The areas of the contaminated territories and the volume of waste were determined. Additionally, data evaluation was performed using the TPT-cloud software suite, which allowed for optimizing the scope of the conducted studies and accurately interpreting the research results to enhance the quality of the restoration works. The study justifies the methods for conducting restoration measures based on the proposed methodology for assessing the feasibility of using biological methods in land reclamation and waste disposal.

1 Introduction

At present, a significant area of industrialised regions is contaminated by organomineral waste. Examples of facilities that have a complex negative impact on the environment and require ecological recovery are areas of oil production and refining, where there are accumulations of hydrocarbon-containing waste, technogenic lenses of oil products are formed and soils in the aeration zone are polluted during operation of facilities, as well as in case of accidents. Such objects also include accumulators of alcohol bard, excessive activated sludge and sediments of primary settling tanks of treatment facilities, solid municipal waste and agro-industrial waste, sludge of water treatment and recycling water supply of various genesis [1-6].

Biological methods are used to recover contaminated areas and to manage organic waste, which have proven to be ecologically and economically efficient. The methods involve treating the environment with a selective microflora - a destructor. Biodegradation of organics is the process of transforming hydrocarbons into harmless compounds naturally by means of various decomposer bacteria which oxidize organic substances inside bacterial cells. A possible way to treat oil-contaminated soil and waste, for example, is to introduce a selective strain of microorganisms and create favourable nutrient, temperature, aeration,

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acid-alkaline conditions in the treated environment. Another way of implementing biological treatment is biothermal composting, which includes the introduction of adapted microorganisms and is accompanied by a successive change of treatment phases. At the same time, there are a number of limitations in their application. Known criteria for the applicability of biodegradation methods include pH range, temperature, petroleum product concentration and do not take into account the presence of particularly toxic compounds that inhibit life. Often, even the application of organic waste treatment and disposal technologies that have positive conclusions of state environmental expertise and take into account various treatment factors does not guarantee site remediation or waste neutralization. Thus, not all contaminated areas and generated waste can be treated using biological methods. Due to the duration of the biodegradation process, a laboratory or industrial study of the feasibility of the method will result in a longer period of time to decide on the method of site recovery or waste neutralisation. Therefore, it is an urgent task to develop a criterion for the applicability of biological methods for the recovery of contaminated areas and the neutralisation of waste.

As typical representatives of areas contaminated by organomineral waste, the paper considers a fuel oil spill, a section of one of the oil storage tanks with considerable soil contamination of the aeration zone, as well as an area contaminated by the placement of distillery stillage.

2 Materials and methods

The choice of objects of study is due to the fact that they describe many characteristic environmental contaminations:

1. Source-driven contaminations that require both cleanup and elimination of the source of impact (fuel oil spill).
2. A contaminated area without an existing source of impact (geo-environment within the boundaries of an oil depot).
3. Areas that are impacted by organomineral waste and that can be recovered when the source is eliminated (distillery bard).

Employees of Samara State Technical University conducted engineering surveys at each of the sites. Some characteristics of the surveyed sites are presented in Table 1.

Table 1 - Characteristics of the survey objects.

№	Site characteristics	Object name		
		Site contaminated by fuel oil spillage	Geo-environment contaminated within the boundaries of the oil depot	Area contaminated by the placement of distillery stillage
1.	Area of contamination, ha	3,0	1,5	42,0
2.	Depth of pollution, m	2,0	5	10
3.	Sources of pollution	Fuel oil	Oiled soil	Distillery bard
4.	Volume of the pollution source, m^3	1 600	300	25 000
5.	Volume of contaminated geo-environment, m^3	4 000	17 000	300 000

As part of the environmental engineering surveys, the biochemical degradation of pollutants in the aqueous extract from the treated environment was assessed for the organomineral waste and environmental components sampled. The assessment of the possibility of application of biological methods for remediation of territories was carried out according to the reduction of chemical oxygen demand (COD) in the aqueous extract from the treated medium when it is aerated together with excessive activated sludge. The course of work, specified in FR.1.39.2001.00283 "Determination of toxicity of water and water extracts from soil, sewage sludge, wastes by mortality and change of fertility of daphnia" was taken as a basis and adapted to the task to be solved - evaluation of the possibility of biological destruction. In parallel, an experiment on biodegradation of selected samples in laboratory containers was carried out.

Electro-tomography, based on difference of rocks, soils by specific electric resistance, was applied for exact determination of pollution sources location boundaries. An automatic electrical survey station "Skala-48K-12", developed at INGG SB RAS, was used to carry out the work. In order to estimate the level of area and depth distribution of pollution, to identify heterogeneous fragments in the geo-environment and to determine their volumes the authors used the principal component analysis (PCA) method, which allowed to simplify data as a result of their projection onto a new space of latent variables (Esbensen, 2005). The method consists in examining the internal structure of the data, finding the latent relationship (correlation) of objects and variables, which makes it possible to identify from a huge number of samples similar in terms of the totality of indicators, and to identify latent relationships between the indicators and their contribution to the differentiation of samples. The TPT-cloud software package was used as the main computing platform (TPT-cloud..., 2021).

The numerical data are collected in matrix X. The rows of this matrix are the samples (347 samples), the columns are the list of definable indicators (22 indicators). Each row of the original table (sample) corresponds to a point on the surface with certain coordinates. Thus, the work aims to use multivariate classification of data to assess the condition of areas and to develop a universal criterion for the applicability of biological methods for remediation of contaminated areas and waste disposal.

3 Results

Based on the results of engineering surveys, the boundaries of contamination spreading and localisation areas of contamination sources were determined. In a number of cases, geophysical survey methods and multivariate data analysis have been applied to accurately establish the boundaries of contamination spreading zones [8].

An example of the application of geophysical methods is an engineering survey for a site contaminated with fuel oil in the Samara region in order to further develop a recovery project. Areas of surface localisation of oil products represented by large and small oil manifestations were identified in the surveyed area. In addition, in the process of surveys we observed nonstationary pollution, periodic occurrence and change of the pollution area, oil product filling of wells drilled in visually uncontaminated areas and where oil products were initially not encountered. These phenomena were associated with the presence of areas of deep, sporadic spreading of oil products in the soils.

It was not possible to reliably determine the volume of contaminated geo-environment by classical engineering survey methods. In order to determine the exact volume of oil products, their depth distribution and to establish the reasons of their release to the surface, geophysical surveys (GPR survey and electrical tomography) were carried out. The trial GPR survey carried out at the site did not reveal inhomogeneous fragments in the investigated geological strata. Electrotomography helped to identify areas of deep distribution of petroleum products. Based on the results of the geophysical surveys, electrotomographic profiles were constructed (Figure 1).

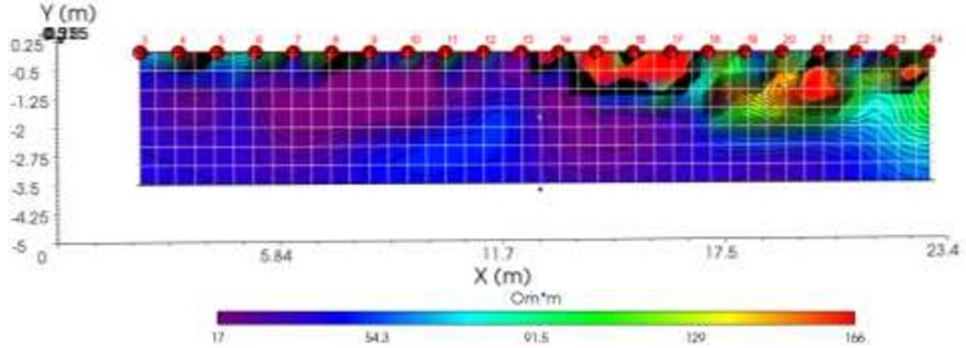

Fig.1. The example of an electrotomographic profile.

The profile traces high resistivity soils from the surface, from electrode 22 to 21 with a depth of up to 1.2m from electrode 18 to 13 with a depth of up to 1.0m. Resistance is 140-180 Ohm*m. Low-resistance soils of 17-50 Ohm*m are underlain by high-resistance soils. The contaminant possesses dielectric properties, which result in the presence of high-resistance zones in geophysical profiles that correspond to the contaminated areas. Tracing the bottom of high-resistance soils on electro-tomography profiles made it possible to assess the spread of polluted soils and identify sources of pollution, which enabled informed project decisions on eliminating sources of pollution.

In a number of cases the classical interpretation of the data does not allow to evaluate the degree of contamination of the territory and determine the volume of geo-environment of different degradation level, taking into account the huge amount of data. The result of the analysis of multidimensional data are the graphs of scores (Fig. 2) and loadings (Fig. 3), which complement each other. The proximity of samples in a graph of scores or indicators in a graph of loadings means that they are generally similar. That is, these graphs show projected relationships between samples in variable (indicator) space. The load plot identifies the reasons why the samples are located on the graph of scores. Essentially, in one coordinate system, there are two graphs: scores (sample distribution) and loads (factors influencing this distribution). The correspondence of sample coordinates and indicator values means that these samples have the highest value of that indicator compared to all other samples. Variables lying in the same direction from the centre are characterised by a positive correlation, those lying in opposite directions by a negative correlation (Esbensen, 2005).

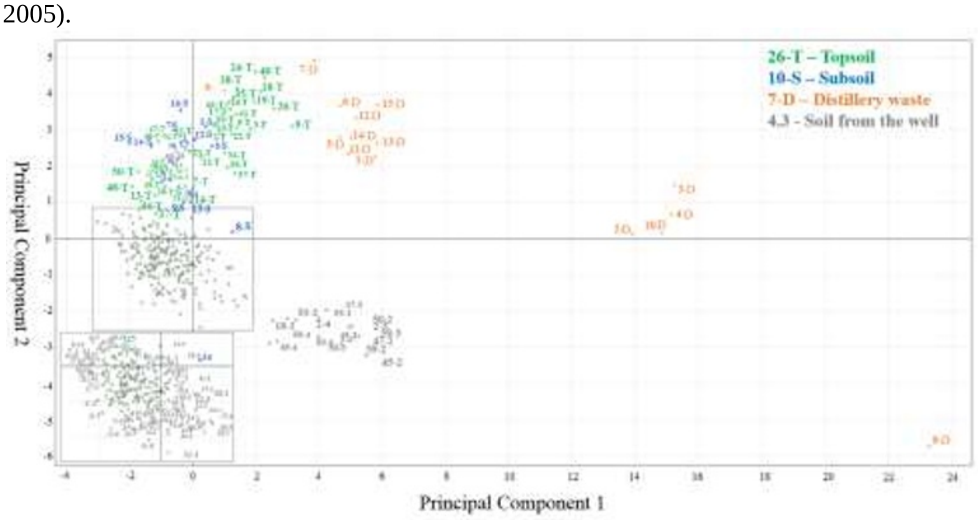

Fig. 2. The graph of PCA scores.

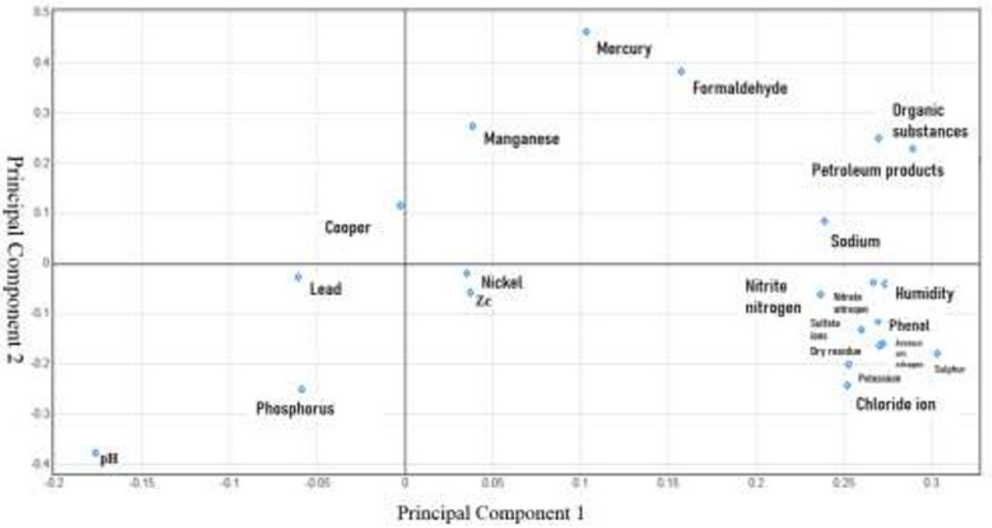

Fig. 3. The graph of PCA loadings.

Application of the method made it possible to differentiate an array of samples according to a set of indicators, to highlight areas of varying degrees of contamination and to identify non-uniform fragments in natural and anthropogenic soils, which are necessary to justify and develop technology for reclamation works, including the management of distillery bard waste. In particular, the selected waste samples were categorized into regions (Fig. 2), which were influenced by the presence of substances such as nitrite, nitrate, and ammonium nitrogen, as well as the content of organic matter, which varied in mineralized and non-mineralized waste (Fig. 3). In accordance with the conducted sample analyses the objects of natural-technogenic environment have been identified, which should be restored or eliminated. Such objects include: 1 - Fuel oil stored on the territory for more than 40 years and being a source of geological environment pollution; 2 - Ground contaminated with fuel oil components; 3 - Contaminated soils of aeration zone on the territory of oil depot; 4 - Distillery bard. Depending on the nature and degree of contamination, different methods can be applied for recovery of the territory: mechanical, chemical, physical-chemical and biological. Considering the organic nature of the contamination, it is preferable to use biological methods. At the same time the disadvantage of biological methods is that not every organic pollution is biodegradable. As part of the work, the possibility of using biological methods for recovery of territories and waste disposal was investigated. The experiment consisted in analysis of COD reduction in aqueous extract from selected samples of waste and contaminated geo-environment when it is aerated in a mixture with excessive activated sludge in a laboratory aerotank. The results of the tests are presented in the graph (Figure 4).

The graph shows the curves of the effects of reduced chemical oxygen demand in the aqueous extracts. The decrease of COD in the aqueous extract from fuel oil was practically not observed. In extracts from samples of contaminated soil COD decreased by more than 70%, which, according to the applied methodology, indicates the possibility of applying biological methods for decontamination and remediation. The COD was also significantly reduced in the alcohol bard extract. Along with the COD reduction effect, the degree of decomposition of ash-free (organic) substance in the respective media was monitored during experimental studies. The reduction of organic substance concentration in contaminated soils and distillery bard during its composting confirmed the possibility of their biological treatment.

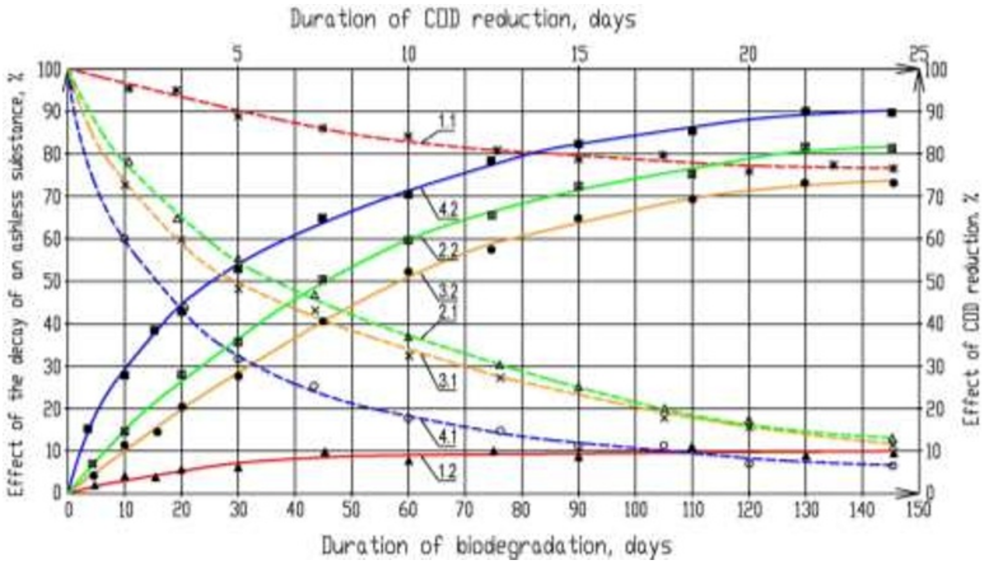

Fig. 4. Results of organic matter biodegradability assessment, Fuel oil (1.1, 1.2), Soil contaminated with fuel oil components (2.1, 2.2), Contaminated soil in the aeration zone at the oil depot (3.1, 3.2), Distillery bard (4.1, 4.2).

4 Discussion

Thus, polluted areas, contaminated soils and grounds, as well as anthropogenic formations that have a negative impact on the environment by washout of polluting substances, are identified on the territory in question. The recultivation of the territory requires, first of all, liquidation of anthropogenic formations. When choosing a method of recultivation various options are considered and the best option is determined on the basis of the evaluation of the planned activity on environmental criteria with regard to possible restrictions determined by the legislation and available technical possibilities. Particularly it is proposed to neutralize the biodegradable waste from the territory with the help of thermal destruction plants. An example of such equipment having a positive conclusion of the state ecological expertise is the "UPNSh-05SD" unit designed for disposal of hazardous oily waste of hazard classes III and IV. For organic wastes of distillery bard, taking into account their high viscosity, it is proposed to excavate them for further treatment within the boundaries of the contaminated area, the waste is treated by means of composting methods. The application of modern technologies for biological neutralisation of organic waste is aimed at obtaining material that can be used for technical recultivation.

The technical phase of the recultivation works includes the construction of a composting site for anthropogenic soils. The developed layout of the temporary site is shown in Figure 5. The main processing facilities are concrete composting cards equipped with air injection and leachate drainage systems (item 10) and treatment facilities (items 7.1-7.4). At the end of the estimated period of distillery bard waste disposal with production of recultivative materials the temporary composting site is dismantled. After the formation of the topsoil layer, biological recultivation of the area is carried out. The biological stage follows the technical stage and includes placement of geotextile on the recultivated surface.

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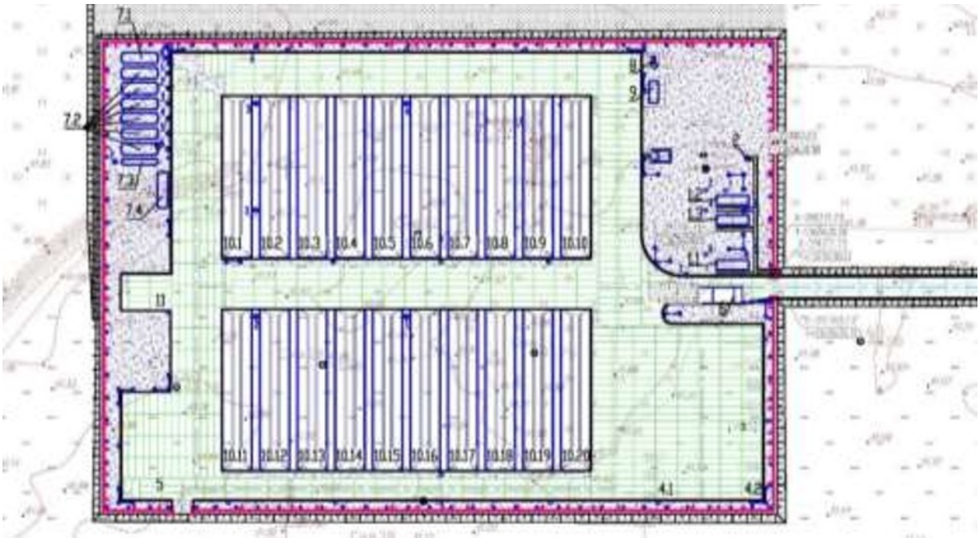

Fig. 5. The plan of the temporary composting site.

Cleaning of the contaminated geo-environment is preferable at the site of its localization and without excavation. For deep cleaning of the geo-environment from oil products the optimal method is ground drainage, which is a kind of in-situ washing with the help of drainage systems that may be combined with the use of oil-degrading bacteria. Examples of such methods implemented in practice by means of the existing patented equipment are a complex for regulated and uniform release of oxygen or other reagents enhancing and supporting the growth of microorganisms necessary for biological cleaning of contaminated territories, developed by the Laboratory of Non-Destructive Testing (LNDT Ltd) [7]. The technology provides a steady, direct diffusion of oxygen into the aquifer through a silicon or PVD tube. The continuous, sequential release of oxygen into the tube creates an optimum concentration in the system, without barbotage and the formation of bubbles from excess oxygen. A limitation of the emitter's application for media cleaning is its operation at depths below the water level. At the same time, most of the surveyed sites have ground contamination from groundwater to the top soilTo clean the geo-environment under such conditions, a bio-ventilation scheme is proposed (Figure 6).

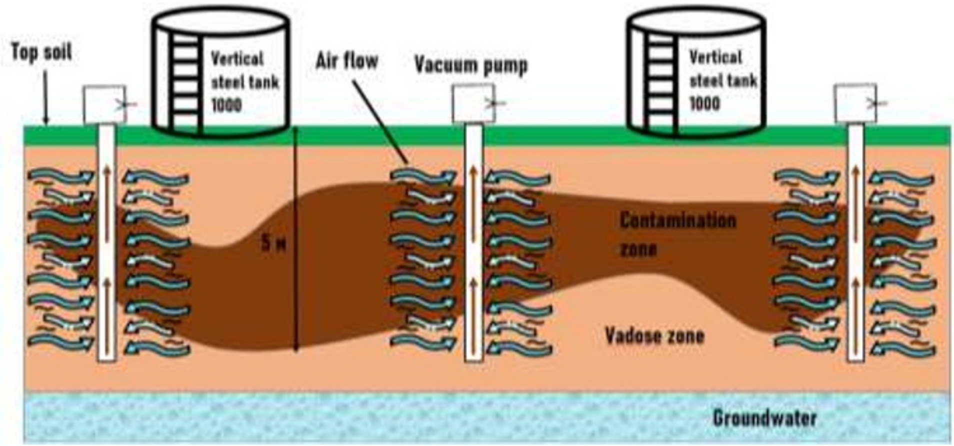

Fig.6. The scheme of bioventilation of contaminated geo-environment.

Bioventilation is a method of oxygenation of the contaminated area. In bio-ventilation, air is injected at a very low flow rate to promote biodegradation. Alternatively, in some cases, the flow rate can be increased to combine pollutant vapour recovery and bioremediation technology. In this case, the contaminants extracted from the vapour phase are treated on the surface by either biological or chemical methods. Wells are constructed around the contaminated area and a vacuum is created to initiate bio-ventilation and accelerate air movement through the contaminated area. This increases the efficiency of oxygen supply throughout the area, and hence the rate of biodegradation of the contaminants. By further increasing the rate of air movement, the contaminants are volatilised and removed as the air passes through the system.

5 Conclusion

Comprehensive assessment of the condition using methods of geophysical research and processing of multidimensional data makes it possible to reliably determine the level of contamination and with high positioning accuracy mark out contamination boundaries. A biodegradation criterion is proposed for the identified fragments of different degree of contamination, which allows assessing the possibility of applying biological methods during land reclamation as well as waste neutralization. The use of the criterion will make it possible to reduce the time for making a decision on the choice of remediation technology from engineering surveys to reclamation works. For each element of the geo-environment the recovery options are proposed, technological schemes of carrying out works with minimal economic costs and maximum ecological efficiency of using biological methods are suggested.

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