Researches about the Decontamination Process of Soils Polluted with Hydrocarbons by Applying the Bioremediation Method – Partial Results

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Abstract

In Romania there are many lands polluted with hydrocarbons, which require decontamination, as they have a significant impact upon the environment and upon the human health. From the decontamination methods, the bioremediation process seems to be quite effective and at the same time it involves low costs. The microorganisms have a very diverse range of metabolic activities for the decomposition of organic compounds that exist in nature. Among the bacteria, *Pseudomonas aeruginosa* is known to have the best capacity to degrade hydrocarbons. The research activities in respect of the identification of the current pollution condition with hydrocarbons of the soil and groundwater, the exact delimitation of the polluted area which requires decontamination were performed in 2010, on Titu site (in Dâmbovița county), a former oil products warehouse, but we also took into consideration the previous investigations (2006, 2009). On the soil and groundwater samples we carried out TPH, BTEX, and PAH tests. Following the interpretation of the tests results, taking into consideration the Order 756/1997, in case of soil, respectively the "Dutch List" in case of groundwater it was found a significant exceeding of the limit values. As we knew the pollution concentrations specific to the soil, the exposure ways and the receivers exposed to the effects, the risk assessment study was performed with the help of the RBCA software application (RBCA Tool Kit 1.3a). The risk assessment study showed the necessity of soil and groundwater decontamination on Titu site, as it is risky both for the environment and for the human health. The soil volume we identified to require decontamination was 3.290 compact m^3 and the groundwater volume to decontaminate was 3.584 m^3.

Keywords: *pollution, hydrocarbons, decontamination, microorganisms, remedial target values*

INTRODUCTION

Like many other European countries, Romania has a long industrialization history. Its result was a significant contamination of the lands and of the groundwater. Land pollution has a significant impact both upon the environment and upon the human health. In terms of environment aspects, pollution can cause a significant deterioration of the environment both by the direct risks upon health which come from the soil and the contamination of some significant resources of the groundwater.

Currently in Romania there is a special interest in the historically polluted sites. At present there is an inventory of 1865 potentially contaminated sites, registered in the CoSIS 2.0 database administered by A.N.P.M. that will include the national inventory of all potentially contaminated sites. This action was initiated in 2007 and the number of sites recorded at present is expected to grow by the strict enforceability of a mandatory declaration scheme.

The growing number of pollutions identified, the more accurate research methods, the discovery

of the action mechanism and the evolution of hazardous substances which cause pollution and last, but not least the practical experiences have led to the development of a wide range of procedures of soil and groundwater decontamination. Thus, in the environment protection decontamination developed gradually in a specific industrial branch, for which there is a growing social and economic demand. On each polluted land the specialists determine based on the local conditions the right technology to be used. The methods in which the natural systems processes are employed to obtain desired results are more often used.

The bioremediation concept includes technologies that use the biological processes for cleaning of polluted soil (soil or groundwater). The bioremediation technologies provide the possibility to decontaminate certain polluted areas with low prices and effectively.

The microorganisms have a wide range of metabolic activities for the decomposition of organic compounds that exist in nature. In the 1950s it was found that all organic compounds formed naturally can be decomposed microbiologically (Kluyver and van Niel 1956). This theory was completed by Alexander (1965) with the observation that the germs have a remarkable adaptation capacity also for the decomposition of synthetic compounds.

The microorganisms which degrade the hydrocarbons pertain to over 100 species and 30 genres. From the bacteria *Pseudomonas aeruginosa* is known to have the best capacity to degrade hydrocarbons.

The hydrocarbons decomposition process by the microorganisms is influenced by environmental factors: temperature, nutrient substances, water, oxygen quantity from soil, etc.

As the HC mixture, namely the oil fuel is a hazardous agent for the environment and health and this particularity is generally accentuated by the artificial additive for the usage purpose, the oil products are classified as hazardous agents, and the industrial secondary products contaminated with them and not used in other purposes are hazardous wastes. From this reason, all activities in the course of which the oil fuel or its derivatives can penetrate in the environment elements and are considered risky activities and potential pollution sources. Soil and groundwater pollution with these compounds may appear during the extraction, processing, transport of various products, their improper storage and distribution etc. Their harmful effect, just like in the case of other environment pollutants depends on the quantity of pollutant which reaches the environment, as well as the properties of the local environment (soil properties, the groundwater level, the precipitation quantities, climate and meteorological factors, the natural and constructed environment). The harmful effects of the hydrocarbons upon the environment can be diverse, as for example (Barótfi, 2000):

Some compounds from the hydrocarbons group can affect the taste and the smell. Thus, percolating the potable water, namely in the surface waters, even in small quantities, such waters are not suitable for consumption.

The volatile compounds can form flammable mixtures, namely explosive with the oxygen in the air.

Some aromatic and poly-aromatic compounds have showed carcinogenic effect, namely they can be toxic and mutagenic. From these, some can have carcinogenic effect also in case of skin absorption (for example the benzene).

By vapour inhaling, they reach the blood and may cause toxic acute reactions, hepatic affections or teratogenic effects.

Infiltrated in the soil and in the groundwater they persist and propagate in the soil for a shorter or longer time depending the hydraulic conductivity of the formation, the content of organic substance and clay, namely their microbiological activity.

Due to the apolar characteristic, the hydrocarbons type of pollutants removes water and the air from the capillaries leading to anaerobic soil conditions.

The average atomic composition of the various types of oil ranges between the following limits, relatively large: 81-87% carbon, 10-14% hydrogen, 0-7% oxygen, 0-6% sulphur, 0-1% nitrogen.

The oil components are classified in three big categories of polluting compounds: total petroleum hydrocarbons (TPH), benzenes and alkylbenzenes (BTEX compounds), respectively polycyclic aromatic hydrocarbons (PAH).

Our research has been carried out since 2010, on a former oil products repository from Titu, Dâmboviţa county, Romania.

The goal of the preliminary research was to identify the current condition of pollution with hydrocarbons of the soil and groundwater, the

exact delimitation of the polluted areas which require decontamination, respectively establishing the remedial target values.

MATERIALS AND METHODS

On the evaluation of the pollution condition and upon drafting the risk assessment study for Titu site (Dâmboviţa county) we took into consideration both the investigations carried out by us in 2010 and those made previously (2006, 2009).

In 2006, for the environmental balance level II, were performed 11 prospection drillings recorded with F1-F11, at different depths: 4,00 m (F7 and F10), 5,00 m (F1, F3, F4, F5, F6, F8, F9 şi F10) and 8,00 m (F2) and they were placed in sensitive areas, predisposed to pollution (even the accidental pollution). The samples were taken from the drillings so as to be able to characterize in a representative manner all levels of rocks encountered and their pollution degree. The sampling was usually made on depth ranges of 1 m up to 2 m, depending on the thickness and nature of the lithology spotted, and this way the entire drilled area was tested (Environmental balance level II, 2007).

In the investigations performed to determine the pollution condition from the autumn of 2009 were performed 15 drillings with the help of the spiral drill. The depth of the drillings sole is unitary, of 5,0m. From the drillings were taken punctual samples, generally from one meter to another, but in most of the cases this rule was diverted (for example 1,5m, 2,5m). The groundwater samples were taken with submersible pump from 15 drillings. Before the samples were taken the hydrostatic level was measured. The TPH and BTEX content was analysed for the groundwater and soil samples (technical-economic study, 2009).

In 2010 we made a number of 35 pits with depth of 2,5-4,0 m, marked with GT-1-35. In the stable formations – clay, rock dust – the pits were deepened up to the aquifer layer. This meant a depth of 2,7-3,5 m. We made the geological description of the stratigraphy discovered in every pit. Also, we recorded the data related to the groundwater level, as well as the changes in color and the smell effect that indicate pollution. We took a total of 70 soil samples and 19 groundwater samples. On these samples we carried out TPH, BTEX and PAH tests.

In order to draft the hydrogeological study we needed information related to the aquifer layer from the site, thus we had to perform another series of drillings. They were made in 2011, recorded with TM-1-8. The wells were fitted so as to be used as monitoring wells during the decontamination process and after that.

The lay-out plan of the sampling points from years 2006, 2009, 2010 respectively 2011 are presented in figure no.1.

The determination of the total content of hydrocarbons from the soil was made by the gravimetric method and by gas chromatography.

As we knew the pollution concentrations specific to the land, the exposure methods and the receivers exposed to the effects, the risk assessment study was performed with the help of the RBCA software application (RBCA Tool Kit 1.3a).

Determination of the remedial target values for soil and groundwater (maximum concentrations of the pollutants in the soil after the decontamination operations) were made based on the results and recommendations of the risk assessment study corroborated with the legislation in force, Order 756/1997 in case of soil, respectively "Dutch list 2000" in case of groundwater.

RESULTS AND DISCUSSIONS

In table 1 are pointed the results of the TPH, BTEX and PAH tests for the groundwater samples made in 2009 and 2010. Following the interpretation of the tests taking into consideration the Dutch List from the total of 15 drillings we found significant exceeding of the limit values in 7 wells, namely: PT2, PT6, PT7, PT8, PT13, PT14, PT15. These wells are located in the area of the former reservoirs platform and in the area of tankers loading pumps. The highest value recorded in the TPH in 2009 was 4.770 µg/l in the well PT15, 8 times higher than the admitted limit of 600 µg/l. In 2010 it was 4.480 µg/l, nearly 8 times above the admitted limit. In case of benzene, the maximum concentration recorded in 2009 was 3.430 µg/l (in the well PT7), 114 higher than the admitted value limit of 30 µg/l. In 2010 it was 348 µg/l in the same PT7 well. A significant exceeding was recorded for xylenes, the maximum concentration recorded in 2009 was 2.630 µg/l, 37 times above the admitted value.

In tables 2 and 3 are presented the results of the TPH tests for the soil samples made in 2010.

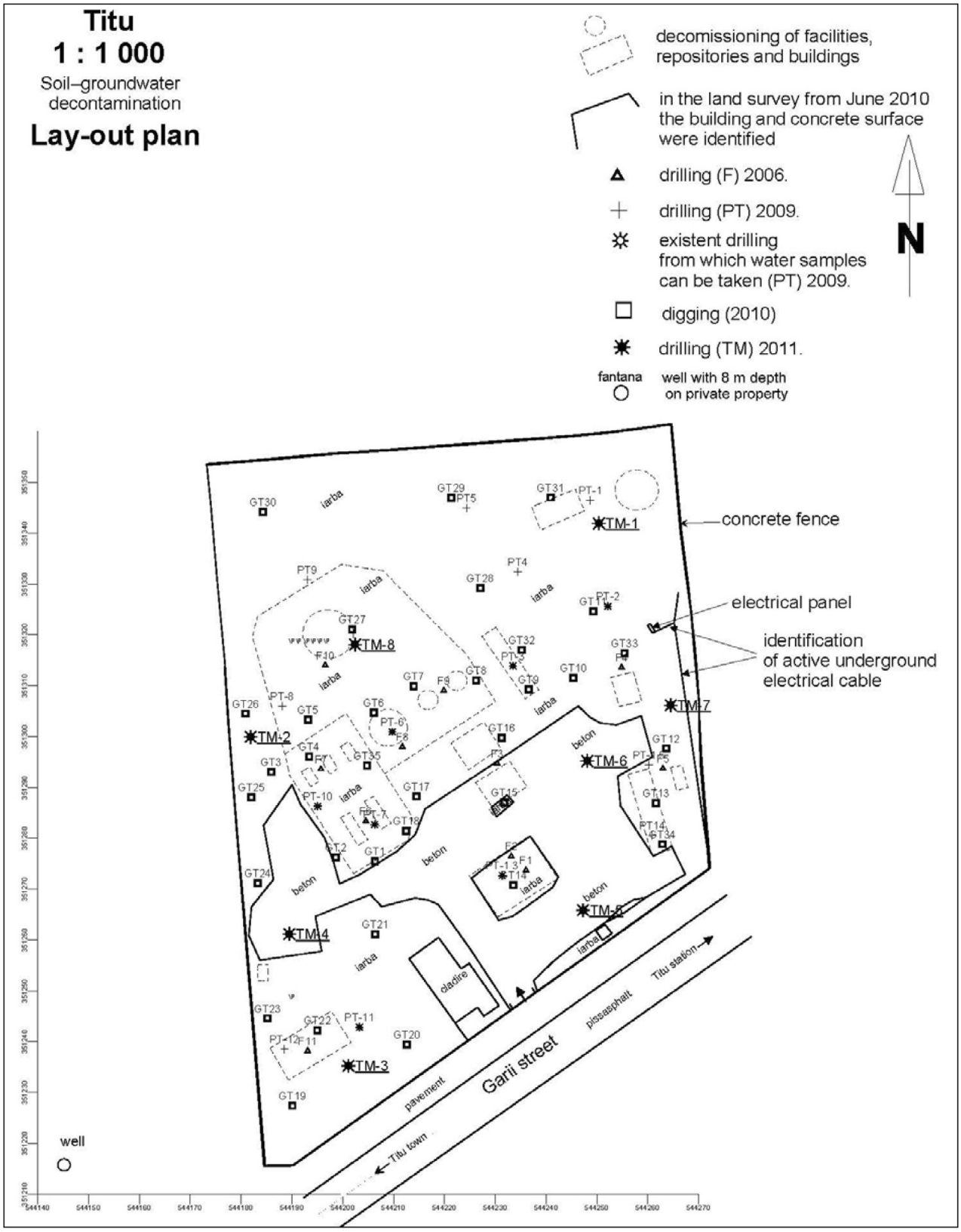

Fig. 1. Lay-out plan of the sampling points (Petz *et al*., 2012)

Tab.1 Test results for groundwater samples

Pollutants			Decontamination limit		Existent drilling from which water samples can be taken															
			Dutch list	Remedial target value	PT-1		PT-2		PT-3		PT-4		PT-5		PT-6		PT-7		PT-8		PT-9	
					2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010
TPH-GC	C5-12	µg/l		400	<10		39	216.0	<10	280.0	<10		<10		1,730	1,140.0	440	1,410.0	70		<10	
TPH-GC	C13-40	µg/l		750	67		3,750	76,7	386	25,9	64		<10		1,380	15,7	3,740	3,070.0	1,270		<10	
TPH-GC		µg/l	600	1150	67		3,790	293	386	306	64		<10		3,110	1,156	4,180	4,480	1,340		<10	
Benzene		µg/l	30	20	<0,1		49.00	2.58	1.60	1.03	0.47		<0,1		660	22.10	3430	348.00	1890		0.28	
toluene		µg/l	1000		<0,1		5.10	1.36	0.94	0.59	0.28		<0,1		502	19.40	164	4.58	115		<0,1	
ethyl-benzene		µg/l	150		0.41		10.00	0.35	0.62	0.21	0.15		<0,1		810	48.60	370	21.70	294		0.32	
xylene		µg/l	70	88.1	1.40		112.00	1.00	30.00	0.57	26.00		<0,1		2630	88.10	1540	50.00	1330		1.50	
other alkylbenzenes		µg/l		300				37.80		26.30			<0,1			198.00		655.00				
naphtalene		µg/l		2.97				0.14		2.97						0.48						
Total PAH without naphtalene		µg/l		1.4				0.07		1.40						0.16						
Total BTEX		µg/l			64		783		217		199		<0,1		8,300		8,190		6,090		9	
Total alkylbenzenes		µg/l			62		607		184		171		<0,1		3,700		2,690		2,470		7	

Pollutants			Decontamination limit		Existent drilling from which water samples can be taken												
			Dutch list	Remedial target value	PT-10		PT-11		PT-12		PT-13		PT-14		PT-15		NPT1
					2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2009	2010	2010
TPH-GC	C5-12	µg/l		400	<10	158.0	<10	1,9	<10		84	1,010	51		46		6.8
TPH-GC	C13-40	µg/l		750	507.0	60,4	60	19,9	<10		2,070	122	1,490		4,720		8.1
TPH-GC		µg/l	600	1150	507	218	60	21,8	<10		2,160	1,130	1,540		4,770		14.9
Benzene		µg/l	30	20	0.52	0.84	0.27	nd	0.20		277.00	183.00	267.00		143.00		<0,1
toluene		µg/l	1000		0.88	0.62	<0,1	nd	<0,1		7.70	2.23	7.60		4.40		<0,1
ethyl-benzene		µg/l	150		0.37	0.14	0.15	nd	<0,1		5.80	1.72	5.90		3.70		<0,1
xylene		µg/l	70	88.1	1.20	1.50	0.78	nd	0.60		13.00	3.88	12.00		7.00		<0,1
other alkylbenzenes		µg/l		300		22.40		nd				98.30					<0,1
naphtalene		µg/l		2.97				0.03									0.091
Total PAH without naphtalene		µg/l		1.4				0.01									0.017
Total BTEX		µg/l			72		12		4		682		1,000		579		
Total alkylbenzenes		µg/l			69		10		4		379		708		420		

nd-non-detectable

Pollutants			Decontamination limit		Water sample taken from the pit											
			Dutch list	Remedial target value	GT-5	GT-10	GT-12	GT-15	GT-16	GT-19	GT-24	GT-25	GT-28	GT-30	GT-31	GT-34
					2010	2010	2010	2010	2010	2010	2010	2010	2010	2010	2010	2010
TPH-GC	C5-12	µg/l		400	7.5	1,560.0	104.0	425.0	346.0	6.1	7.2	74.7	9.6	6.8	18.4	6.0
TPH-GC	C13-40	µg/l		750	25.6	435.0	51,9	2,570.0	145.0	30.8	46.8	34.8	35.8	18.3	42.0	43.2
TPH-GC		µg/l	600	1150	33.1	2,020.0	156.0	3,000.0	491.0	36.9	54.0	110.0	45.4	25.1	60.4	49.2

Tab. 2 Concentration of total petroleum hydrocarbons (TPH) measured in the soil samples taken in 2010

Measurement spot GT-1-35	Total petroleum hydrocarbons (TPH)	h [m]	C_{TPH} [mg/kg]
1	C5-12	-0,5	129
		-1,8	**559**
		-2,5	**548**
	C13-40	-0,5	1170
		-1,8	1660
		-2,5	1730
	C5-40	-0,5	1300
		-1,8	**2220**
		-2,5	**2280**
2	C5-12	-0,5	367
		-2,0	183
	C13-40	-0,5	**3240**
		-2,0	1180
	C5-40	-0,5	3610
		-2,0	1360
4	C5-12	-2,3	5,1
	C13-40	-2,3	69,8
	C5-40	-2,3	74,9
5	C5-12	-2,2	2,2
	C13-40	-2,2	58,8
	C5-40	-2,2	61,0
6	C5-12	-1,5	**1190**
	C13-40	-1,5	1170
	C5-40	-1,5	**2360**
7	C5-12	-2,3	**413**
	C13-40	-2,3	338
	C5-40	-2,3	751
8	C5-12	-2,2	17,0
	C13-40	-2,2	22,6
	C5-40	-2,2	39,6
9	C5-12	-1,9	377
	C13-40	-1,9	1190
	C5-40	-1,9	1570
10	C5-12	-1,7	**861**
	C13-40	-1,7	**3250**
	C5-40	-1,7	**4110**
11	C5-12	-2,0	**473**
	C13-40	-2,0	1490
	C5-40	-2,0	1960
12	C5-12	-2,1	347
	C13-40	-2,1	1500
	C5-40	-2,1	1850

Tab. 3 Concentration of total petroleum hydrocarbons (TPH) measured in the soil samples taken in 2010

Measurement spot	Total petroleum hydrocarbons (TPH)	h [m]	C_{TPH} [mg/kg]
13	C5-12	-1,5	0,9
		-2,2	368
		-3,4	25,9
	C13-40	-1,5	50,2
		-2,2	**2510**
		-3,4	176
	C5-40	-1,5	51,1
		-2,2	**2880**
		-3,4	202
14	C5-12	-2,7	**606**
	C13-40	-2,7	1290
	C5-40	-2,7	1900
15	C5-12	-0,6	613
	C13-40	-0,6	2810
	C5-40	-0,6	**3420**
16	C5-12	-1,2	**667**
	C13-40	-1,2	**3640**
	C5-40	-1,2	**4310**
25	C5-12	-0,6	134
	C13-40	-0,6	**7530**
	C5-40	-0,6	**7660**
27	C5-12	-2,0	0,9
	C13-40	-2,0	8,3
	C5-40	-2,0	9,2
28	C5-12	-1,6	0,6
	C13-40	-1,6	4,8
	C5-40	-1,6	5,4
32	C5-12	-1,7	**469**
	C13-40	-1,7	1460
	C5-40	-1,7	1930
33	C5-12	-1,4	**792**
	C13-40	-1,4	**2200**
	C5-40	-1,4	**2990**
34	C5-12	-2,4	14,1
	C13-40	-2,4	132,0
	C5-40	-2,4	146,0
35	C5-12	-1,6	**578**
	C13-40	-1,6	**2000**
	C5-40	-1,6	**2580**

Tab. 4 Remedial target values established to be obtained at the end of the remedial program

Pollutants	Remedial target values	
	ground water	soil
	µg/l	mg/kg
TPH C5-12	400	400
TPH C13-40	750	1900
TPH total petroleum	1150	2000
Benzene	**20**	
Xylene	88,1	0,15
Other alkylbenzenes	300	5
Total naphthalene	2,97	2,15
PAH total without naphthalene	1,4	1,22

Following the results interpretation, taking into consideration the Order 756/1997, were recorded significant exceeding of the intervention thresholds (type of use less sensitive) in the samples taken from the following pits: GT1 (samples taken from the depth range 1,1-2,0 m and 2,1-3,0 m); GT2 (0,0-1,0m); GT6 (1,1-2,0m); GT10(1,1-2,0m); GT13 (2,1-3,0m); GT16 (1,1-2,0m); GT17 (0,0-1,0m); GT18 (1,1-2,0m); GT25 (0,0-1,0m); GT33 (1,1-2,0m); GT35 (1,1-2,0m). They are located in the area of the former reservoir platform, in the area of the former grease separating tank, in the area of the former pumps and distribution stations. The highest TPH concentration was recorded in the soil sample taken from pit no. GT25 from the depth range 0,0-1,0m, being of 7.660mg/kg, nearly 4 times above the intervention threshold, of 2.000 mg/kg (Petz *et al*., 2012).

In the risk assessment study, based on the data concerning the site pollution condition, the possible receivers, the pollutants reaching the receivers on various ways with the RBCA software, we calculated the target values for the soil and groundwater (for lands with industrial use). The remedial target values were established based on the target values calculated in the risk assessment study for the compounds with risk for health and taking into consideration the requirements of Order no.756/1997. They are listed in table 4. The total petroleum hydrocarbons with C_5-C_{40} atomic number were separated during the risk analysis in aromatic and aliphatic hydrocarbons with C_5-C_{12} (VPH) atomic number, respectively monoaromatic aliphatic hydrocarbons with C_{13}-C_{40} (EPH) atomic number. This separation was necessary due to the difference of the risk represented for health. The risk of the volatile aromatic hydrocarbons is much higher than that of the aliphatic hydrocarbons (Dura *et al*., 2010).In respect of the hydrogeological information of the researched site, we could say that based on the diggings made and based on the literature information the main aquifer formation is the fluvial sand sediment, sand with gravel, gravel with sand of Pleistocene Holocene age, carried down by the waters descending from the Carpathians. Considering the diggings, this aggregation of detrital sediments is replaced at the middle of the site towards the east by an alluvial aggregation, more bound, from rock dust, argillaceous rock dust, clay with rock dust. Its thickness varies between 3,0-5,5 m. Under the aquifer formation there is a compact layer of clay, clay with rock dust, of green colour. Above the aquifer layer there is an alluvial formation thick of 1-2,6 m, covered in a mixed filling with variable thickness (on average 0,5 m) (Petz *et al*., 2011).

CONCLUSIONS

The risk assessment study showed the need to decontaminate the soil and the groundwater on Titu location, as it was risky both for the environment and for the human health.

We established the remedial target values to be reached after the decontamination activities for the following pollutants: TPH, BTEX and PAH.

Bioremediation is the technology established for the site decontamination, taking into consideration the local specific conditions and the type of pollutants. Besides the fact it provides cheap and effective decontamination for certain soils, it does not have a negative effect upon the environment, no hazardous waste occurs in comparison to the other decontamination methods;

The volume of polluted soil we identified to decontaminate is 3.290 compact m^3, the area projected on the surface is 2.130 m^2. The volume of the groundwater mass to decontaminate is 3.584 m^3.

REFERENCES

1. Alexander, M.: 1965, Biodegradation: problems of molecular recalcitrance and microbial fallibi- lity., Advances in Applied Microbiology 7, 35-80.
2. Barótfi, I. (2000) Környezettechnika, Mezőgazda Publishing House, Budapest, 571-588.
3. Dura, Gy., Mensáros, P., Petz, R. (2010). Risk assessment study, 40-42.
4. Kluyver, A. andi van Niel, C.: 1956, The microbe's contribution to biology, Harvard University Press.
5. Petz, R., Mensáros, P., Niszler, B., Szabó, P., Hening Helga (2012), Technical project for the procurement of water management permit, 7-19, 22-31.
6. Petz, R., Mensáros, P., Hening Helga (2011), Hydrogeologic study, 12-15.
7. *** Ord. 756/03.11.1997 for the approval of Regulation regarding the assessment of environmental pollution
8. ***"Dutch List 2000" concerning the limits for the indicators concentration in the groundwater, accepted in the European Community
9. ***National strategy for the management of contaminated sites
10. ***Environmental balance level II for the closing of Titu landfill, Dâmboviţa county, 2007, 7-19.
11. ***Technical-economic study for the determination of polluted area and the optimal method to decontaminate the soil and the groundwater from Titu landfill, 2009, 17-22.