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Remediation Measures for Poşta Rât Contaminated Site (Turda)

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Abstract

Waste (in the form of isomers of hexachlorocyclohexane - HCH) resulting from the fabrication process of lindane of the former UCT - Turda Chemical Plants were stored, from 1954 to 1983, in 4 uncontrolled settlements from the Turda area, one of which is the settlement from the Posta Rât. Posta Rât contaminated site occupies an area of 4 hectares, outside the built-up area of the Turda Municipality, on the left side of Aries River, summing up a quantity of approximately 18 500 tons of waste mixed with soil. As a result of uncontrolled storage activities, the water, air, soil and biodiversity were affected. Due to the strong negative influence of this historically contaminated site, in this material our attention focuses on environmental impact assessment and identifies the most appropriate measures for the site rehabilitation in order to restore soil functions. Based on the soil and groundwater analysis, the following measures were proposed in order to ensure human health and environmental protection: on-site treatment of contaminated soil and groundwater, laying clean vegetal ground throughout the entire surface and replanting the retrieved land's surface with trees. To ensure the success of rehabilitation action is required to install a ground water monitoring network and carrying out a monitoring plan.

Keywords: contaminated site, pesticides, remediation measures

1. Introduction

The impact of anthropogenic activities on the soil quality has been strongly enhanced during the last few decades due to the population growth and an extensive exploitation of natural resources including soils. Following processes may be mentioned as the main source of the increased impact on the soil quality: atmospheric depositions originating mainly in industrial and traffic emissions, agricultural technologies – especially the use of organic and mineral fertilizers and pesticides, waste applications to soils including anthropic fluvial loads (an application of sewage sludge seems to be one of the most important source of soil pollution in the present time), old uncontrolled deposits and natural geogenic loads (1).

All these impacts may affect soil microorganisms in many different ways, direct and indirect, as well. Some organisms cannot survive, other develop adaptive mechanisms, a part remains unaffected, new organisms get favoured in the new modified ecosystem. As a consequence of this, composition of soil biodiversity may undergo change which may harm the basic ecological soil functions (2).

Pollution and the risks for the human communities or natural ecosystems continue even if the activities that produced the degradation of the land have been ceased. These areas remain a continuous source of risk and pollution (3). Not taking into account these risks can lead sometimes to accidents that have a great impact from the

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ecological point of view or direct consequences on human communities.

Such events happened in other countries as well; therefore the authorities have made real codes of rules for the investors so that development should not have a destructive impact on the land. Inventories were made of such land contaminated with proposals for remedial techniques and possible future use.

The aims of the present study are the investigation of the impact of hexachlorocyclohexane waste deposit from Turda on soil and groundwater and identifying the most appropriate methods of land remediation. This approach may permit an evaluation of the status of polluted ecosystems, while providing insight about the accumulation and transformation processes of pollutants in soil and groundwater.

2. Material and Method

Soil and groundwater samples. Soil samples were taken from Poşta Rât contaminated site, an area of 4 hectares, outside the built-up area of the Turda Municipality, on the left side of Arieş River. Individual soil cores were taken with a PVC core sampler (at a depth of 0-1 m) from three different places and mixed together to prepare a composite sample for each site. The composite samples were used for all subsequent analyses. Groundwater sample was taken from the monitoring wells on the site.

Chemical analyses. The pH values were determined with Jenway – Ion-Meter 3340 pH meter; conductivity with HANNA HI 993310 conductivity meter, organochlorine pesticides, polychlorinated biphenyls, benzene, toluene, ethylbenzene, and xylenes (BTEX), *v*olatile organic compounds (VOC) and oil products concentrations by gas chromatography-mass spectrometry. Gas chromatography was performed using a Agilent Technologies 5975 B VL MSD mass spectrometer. Metals concentrations were analyzed with atomic absorption spectrophotometer Perkin-Elmer SCIEX ICP -MS type ELAN DRC II and ion concentration (nitrates, nitrites, chlorides, sulphures, total cyanides), by molecular absorption spectrometry using a spectrometer Perkin Elmer type BX I.

3. Results and Discussions

Chemical analyses were performed to determine the type and concentration of pollutants in order to identify the most appropriate techniques of land remediation. The interpretation of the results from chemical analyses on soil samples taken from the Poşta Rât site was carried out in conformity with Order number 756/1997 of the Ministry of Waters, Forests and Environmental Protection, which establish the normal, alert and intervention concentrations of polluting agents in the soils for sensitive use or less sensitive use (industrial). The chemical characteristics of the analysed soil samples are presented in the tables 1- 3.

Table 1 shows the presence in the soil samples of all analysed heavy metals. The concentrations of Zn, Pb, Cu, Hg and As were higher than the normal limits. The Pb, Cu and As concentrations exceeded alert concentrations of soils for sensitive use and As concentration was much more over the intervention limit, which represents an alarm signal for human and environmental health. The highest exceeded normal values were recorded for As, Cu, Pb and Hg. The normal values were exceeded by 27.5 times for As, by 7.3 times for Cu, by 4.6 times for Pb and by 4.5 times for Hg.

The concentrations of Cd, Ni and Cr were significantly below the normal limit. Also, the concentration of oil products has not exceeded the limit value according Order 756/1997.

The results obtained showed a strong contamination of soil with organochloride pesticides (hexachlorocyclohexane), the limits stipulated in Order No. 756/1997 were exceeded for all analyzed pesticides. The highest exceeded of normal values were recorded for α-HCH isomer (by 1240 times), β-HCH isomer (by 840 times) and γ-HCH isomer (by 500 times).

The concentrations of PCB 28, PCB 52, PCB 101 and PCB 153 were higher than the normal limits but the concentrations of all analysed polychlorinated biphenyls were below the alert and intervention limit according to the Order number 756/1997 of the Ministry of Waters, Forests and Environmental Protection - Regulation regarding evaluation of environment contamination.

The highest exceeded normal values were recorded for PCB 52, PCB 28 and PCB 101. The PCB 52 concentration exceeded the normal values by 6.6 times, the PCB 28 concentration exceeded the normal values by 4.1 times and the PCB 101 concentration exceeded the normal values by 1.2 times. The groundwater quality was evaluated by analyzing a sample of water taken from the monitoring wells of the phreatic layer.

Due to the lack of regulations on the quality of groundwater, the results of the analysis were compared with values of the maximum allowable in accordance with Law number 458/2002 on the quality of drinking water, amended by Law number 311/2004.

Table 1. Concentrations of oil products and heavy metals in polluted soil from Poşta Rât

Order no. 756/1997	Oil products	Zn	Cd	Pb	Ni	Cu	Cr	Hg	As
	Measurement unit (ppm)								
Criterion a	<100	100	1	20	20	20	30	0,1	5
Criterion b	200	300	3	50	75	100	100	1	15
Criterion c	500	600	5	100	150	200	300	2	25
Soil sample	< 20	260	0.5	92.23	8.93	145.8	21.16	0.45	137.4

Criterion a – normal values, Criterion b – alert concentration of soil for sensitive use, criterion c – intervention concentration of soil for sensitive use

Table 2. Concentrations of organochloride pesticides in polluted soil from Poşta Rât

Order no. 756/1997	α-HCH	β-HCH	γ-HCH	δ-HCH	ε-HCH	Total - HCH
	Measurement unit (ppm)					
Criterion a	<0.002	<0.001	<0.0001	<0.001	-	<0.005
Criterion b	0.1	0.05	0.02	0.05	-	0.25
Criterion c	0.2	0.1	0.05	0.10	-	0.5
Soil sample	2.48	0.84	0.05	0.12	0.03	3.52

Table 3. Concentrations of polychlorinated biphenyls in polluted soil from Poşta Rât

Order no. 756/1997	PCB 28	PCB 52	PCB 101	PCB 153	PCB 180	PCB 194
	Measurement unit (ppm)					
Criterion a	<0.0001	<0.0001	<0.0004	<0.0004	<0.0004	-
Criterion b	0.002	0.002	0.01	0.01	0.01	-
Criterion c	0.01	0.01	0.04	0.04	0.04	-
Soil sample	< 0.00041	< 0.00066	< 0.00049	< 0.00046	< 0.00027	< 0.00024

The concentrations of nitrates, chlorides, sulphures, sodium, mercury, total polycyclic aromatic hydrocarbons (PAH) and pesticides (α-HCH and β-HCH) were higher than the maximum allowed concentration stipulated by Law 458/2002 and Law 311/2004 regarding drinking water quality.

The highest exceeded of MAC were recorded for PAH (by 32.3 times), pesticides (by 17.5 times), Na (by 16.4 times), Cl^- (by 13 times) and Hg (by 12 times). The results of chemical analysis of soil and groundwater samples showed the following risks for the environment and human health:

- Underground and surface water contamination risk through leakage, infiltration and migration of the contaminants from the storage facility;
- Risk for the human health of resident inhabitants from the settlement's vicinity through the inhalation of dust containing contaminants, raised from the storage facility during windy periods;
- Risk for the human health of resident inhabitants from the settlement's vicinity through epidermal contact, direct ingestion through fruits/vegetables that assimilate the identified contaminant (HCH).

For the interruption of identified source-means-receiver contamination relations which were associated to the risk for human health and environment, urgent remedial actions are needed. Remedial options should cover: the elimination or treatment of the source of pollutants; the elimination or modification of means of transmission and the elimination or modification of the receivers' behaviour.According to the results of chemical analysis of soil and groundwater samples were identified the most feasible remedial technologies (table 5). According to the above mentioned, for the selection of soil remedial technologies the following methods remain feasible:

- Engineering methods (removal and/or solutions for limiting pollutants);
- Removing the source by combustion and storage outside the site;
- Changing the method of transmission including the thermal treatment on site and re-using the soil as filling.

For aquifer remediation we consider feasible the following methods:

- Engineering methods – hydraulic barriers, barriers of soil insulation;
- Physical method – permeable reactive barriers;
- Pumping and treatment;
- Biological method – monitoring natural reduction (passive approach).

Table 4. Concentrations of pollutants in groundwater from Poşta Rât

No.	Indicators	M U	Determined values	Maximum allowed concentration (MAC) Law 458/2002 Law 311/2004
1.	The concentration of hydrogen ions, pH	pH unit	7.51	6.5 – 9.5
2.	Conductivity at 20^{0}C	µS /cm	10680	2500
3.	Total cyanides (CN)	µg /dm^3	< 0.05	50
4.	Nitrates (NO_3^-)	mg /dm^3	57.5	50
5.	Nitrites (NO_2^-)	mg /dm^3	< 0.05	0.5
6.	Chlorides (Cl^-)	mg /dm^3	3270	250
7.	Sulphures (SO_4^{2-})	mg /dm^3	1030	250
8.	Boron (B)	mg /dm^3	< 0.07	1
9.	Cadmium (Cd)	µg /dm^3	< 1	5
10.	Total Chrome (Cr_T)	µg /dm^3	27.50	50
11.	Total Copper (Cu_T)	mg /dm^3	0.02	0.1
12.	Nickel (Ni)	µg /dm^3	< 5	20
13.	Lead (Pb)	µg /dm^3	< 3	10
14.	Potassium (K)	mg /dm^3	160	–
15.	Sodium (Na)	mg /dm^3	3285	200
16.	Zinc (Zn)	µg /dm^3	116	5000
17.	Mercury (Hg)	µg /dm^3	11.95	1
18.	Total polycyclic aromatic	µg /dm^3	1.81	0.1
	hydrocarbons	µg /dm^3	0.13	–
	(PAH): – pyren	µg /dm^3	1.29	–
	– **c**risen	µg /dm^3		0.01
	– benz-a pyren			
19.	Volatile organic compounds (VOC):	µg /dm^3	1.80	
	– CCl_4	µg /dm^3	< 9.3	
	– CH_2Cl_2	µg /dm^3	< 0.075	100
	– $CHCl_3$			
20.	BTEX (benzene, toluene, ethylbenzene, and xylene)	µg /dm^3	2.73	–
21.	Total oil products	mg /dm^3	< 0.02	–
22.				–
	PCB (polychlorinated biphenyls):	µg /dm^3	< 0.001	
	– PCB 28	µg /dm^3	< 0.0016	
	– PCB 52	µg /dm^3	< 0.0012	
	– PCB 101	µg /dm^3	0.0015	
	– PCB 153	µg /dm^3	< 0.0007	
	– PCB 180	µg /dm^3	< 0.0006	
	– PCB 194			
23	Pesticides:			0.5
	– α-HCH	µg /dm^3	7.02	
	– β-HCH	µg /dm^3	1.54	
	– γ-HCH	µg /dm^3	0.08	
	– δ-HCH	µg /dm^3	0.05	
	– ε-HCH	µg /dm^3	0.09	
	– Suma HCH	µg /dm^3	8.78	

Table 5.The matrix of applicable retrieval options

	ORGANIC SUBSTANCES							
		Applicable for the following substances						
Retrieval options	**Application environment (ground or water)**	Volatile Organic Compounds (VOC)	Halogenated hydrocarbons	Non-halogenated hydrocarbons	Polycyclic aromatic hydrocarbons	PCB	Furan and Dioxin	Pesticides and herbicides
ENGINEERING METHODS								
Limiting - shut down systems	S	√	√	√	√	√	√	√
Limiting - hydraulic barriers	A	√	√	√	√	√	√	√
Limiting - insulation barriers in the ground	S, A	√	√	√	√	√	√	√
Excavation and storage	S	√	√	√	√	√	√	√
BIOLOGICAL METHODS								
Natural attenuation	A	√	√	√	√	X	X	√
Biopile	S	√	X	√	√	X	X	√
Bio-ventilation	S	√	√	√	√	X	X	X
Bio-degradation through air injection	S, A	√	√	√	√	X	X	√
Spreading on agricultural land	S	√	X	√	√	X	X	√
Bio-treatment with the sludge phase	S	√	√	√	√	X		√
Biological degradation	S	√	X	√	√	X	X	√
CHEMICAL METHODS								
Chemical oxidation	S, A	√	√	√	√	X	X	√
Chemical dehalogenation	S	√	√	X	X	√	√	X
Spray ground washing	S	√	√	√	√	X	X	X
Extraction with solvents	S	√	√	√	√	√	√	√
Land improvements	S	X	X	X	X	X	X	X
PHYSICAL METHODS								
EVS dual phase	S, A	√	√	√	X	X	X	X
Air injection	A	√	√	√	X	X	X	X
Vapour extraction from the ground (EVS)	S	√	√	√	X	X	X	X
Reactive permeable barriers (BPR)	A	√	√	√	√	√	√	√
Ground washing	S	X	√	√	√	√	X	√
STABILIZATION AND SOLIDIFICATION METHODS								
Hydraulic binders (such as: cement)	S	X	X		√	√	√	
Vitrification	S	√	√	√	√	√	√	√
THERMAL METHODS								
Incineration	S	√	√	√	√	√	√	√
Thermal resorption	S	√	√	√	√	√	X	√

INORGANIC AND EXPLOSIVE SUBSTANCES						
		Applicable for the following substances				
Retrieval options	**Application environment (ground or water)**	Heavy metals	Non-metals	Asbestos	Cyanides	Explosives
ENGINEERING METHODS						
Limiting - shut down systems	S	√	√	√	√	√
Limiting - hydraulic barriers	A	√	√	√	√	√
Limiting - insulation barriers in the ground	S, A	√	√	√	√	√
Excavation and storage	A	√	√	√	√	√
BIOLOGICAL METHODS						
Natural attenuation	A	√	√	X	X	√
Biopile	S	X	X	X	X	√
Bio-ventilation	S	X	X	X	X	X
Bio-degradation through air injection	S, A	X	X	X	X	X
Spreading on agricultural land	S	X	X	X	X	√
Bio-treatment with the sludge phase	S	X	X	X	√	√
Biological degradation	S	X	X	X	X	√
CHEMICAL METHODS						
Chemical oxidation	S, A	X	√	X	X	X
Chemical dehalogenation	S	X	X	X	X	X
Spray ground washing	S	√	X	X	X	X
Extraction with solvents	S	X	X	X	X	√
Land improvements	S	√	√	X	X	X
PHYSICAL METHODS						
EVS dual phase	S, A	X	X	X	X	X
Air injection	A	X	X	X	X	X
Vapour extraction from the ground	S	X	X	X	X	X
Reactive permeable barriers	A	√	√	X	√	√
Ground cleaning	S	√	√	X	√	X
STABILIZATION AND SOLIDIFICATION METHODS						
Hydraulic binders	S	√	√	√	?	X
Vitrification	S	√	√	√	√	√
THERMAL METHODS						
Incineration	S	√	√	√	√	√
Thermal resorption	S	√	X	X	√	X

Consequently, the remediation will include cleaning the site to an appropriate standard for its use as an open public space as well as solving environmental impact problems caused by the historical activities, which were carried out on the site. Site rehabilitation will include on-site treatment using the thermal desorption technique, laying on vegetal soil on the entire surface and re-planting the surface of the land remedied with trees. Also, is needed to be installed an underground water monitoring network fitted for pumping and water treatment in a mobile plant on site (at least for 12 months). The remediate site will be monitored to eliminate any risk to the environment and human health.

4. Conclusions

The results of the elaborated study on contaminated soil from Poşta Rât show that the following indicators overshoot the normal limit: Zn, Pb, Cu, Hg, As, polychlorinated biphenyls and organochloride pesticides, according to the Order number 756/1997 of the Ministry of Waters, Forests and Environmental Protection.

Uncontrolled storage of waste on Poşta Rât site led to groundwater pollution. The chemical analysis revealed high concentrations of nitrates, chlorides, sulphures, sodium, mercury, total polycyclic aromatic hydrocarbons (PAH) and pesticides (α-HCH and β-HCH) in groundwater from Poşta Rât, much more over the maximum allowed concentration stipulated by Law 458/2002 and Law 311/2004 regarding drinking water quality.

The storage facility's uncontrolled nature has allowed the HCH contaminant's migration outside the site by air and (surface/underground) water and its transfer in the food chain, with serious negative effects on human health and environment.

Based on the soil and groundwater analysis, the following measures were proposed in order to ensure human health and environmental protection: on-site treatment of contaminated soil and groundwater, laying clean vegetal soil throughout the entire surface and replanting the retrieved land's surface with trees.

To ensure the success of rehabilitation action is required to install a ground water monitoring network and carrying out a monitoring plan.

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