ORIGINAL PAPER

ASSESSMENT OF HEAVY METALS CONTENT OF CRUDE OIL CONTAMINATED SOIL

CRISTIANA RADULESCU [1], CLAUDIA STIHI[1]. ION V. POPESCU [2.3.4], LUCICA GRIGORA TOMA[2], ELENA DANIELA CHELARESCU[4.5], RALUCA STIRBESCU[5]

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Abstract. *The concentrations of several heavy metals including Pb, Cd, Cr, Cu and Zn in crude oil contaminated soil samples collected from five oil extraction parks of Dambovita County (i.e. Doicesti, Sotanga, Gheboieni, 2 AR Moreni and 2EPS Moreni) owned by SC OMV Petrom were investigated. The samples were collected in November 2011, from two depths (0-5 cm and 30 cm) and were analyzed by EDXRF technique. The higher concentrations of Pb, Cd, Cu, Cr and Zn were found in all polluted soil samples, thus exceeding the MAL values specified in Romanian legislation. According with these data, it can conclude that each analyzed heavy metal can cause pollution of soil with dangerous implication concerning the environment and health.*

Keywords: *heavy metal, crude oil, contaminated soil.*

1. INTRODUCTION

Environmental pollution with oil organic compounds and heavy metals, which are very toxic and relatively accessible, has become a global phenomenon. Contaminated soils from oil extraction activities include a lot of complex organic compounds such as alkanes, benzene, methylbenzene etc, and heavy metals as well. These contaminants are dangerous to the health of all life forms, including humans because usually are categorized as carcinogenic substances. They can not be easily eliminated from soils and frecvently these contaminants will leach into the groundwater systems.

Therefore the soil is the most precious capital of which the humans dispose to satisfy all needs and ambitions. Hence, at least to the invention of artificial photosynthesis, all depending by thin and fertile layer of the Earth's surface, where the resources are extracted whole life [1-5]. On national level, predominant is the ascending pollution with crude oil which is due to pipelines breakage under pressure, leakage from these may reach to the groundwater. Retention capacity in soil of petroleum products depends by the soil content; these products can infiltrate up to 70-80 cm depths and even more, preventing the depollution. It is well known [6-10] that an important indicator which shows the retention of these products in soil is the carbon / nitrogen ratio. Physical processes, which occur due to the crude oil extraction activities, consist in disturbance of soil fertile layer from extraction parks (e.g. surface excavation, electrical network, pressure pipes and cables buried or/on the soil surface

[1] Valahia University of Targoviste, Faculty of Sciences and Arts, 130082 Targoviste, Romania.
E-mail: radulescucristiana@yahoo.com.
[2] Valahia University of Targoviste, Multidisciplinary Research Institute for Sciences and Technologies, 130082 Targoviste, Romania.
[3] Academy of Romanian Scientists, 050094 Bucharest, Romania. E-mail: ivpopes@yahoo.com.
[4] Horia Hulubei National Institute of Physics and Nuclear Engineering, 077125 Magurele, Romania.
[5] University of Bucharest, Faculty of Physics, Doctoral School, 050107 Bucharest, Romania.

etc). All these have as result a compacted soil, with new properties due to specified activities of crude oil extraction process, which it is not benefiting for environment and life as well.

It is well known that in the last years on Dambovita County have been reported some accidentally pollution of soil with crude oil. Some of that were produced around of Moreni city and Morteni village, as well as around of Ocnita and Sotanga village. Hence these pollutions were characterized by salted water and crude oil due to the pipeline breakage. Therefore in 2011, by pipeline breakage around Moreni city have been affected over 1000 m^3, of which 800 m^3 of public utility land and 200 m^3 owned land. Some of protection measures aimed the execution of hinges; oil was collected in position holes, then was emptied and finally was performed the stripping of damaged soil and replacement with farmland.

The main goal of the present study was to use EDXRF technique in order to determine the heavy metals level of crude oil contamined soil, in the vicinity of oil extraction parks from Dambovita County, Romania and to compare the elemental concentrations with the maximum admitted levels (MAL) by the Romanian legislation.

1.1. SITE DESCRIPTION

Oil **E**xtraction **P**ark **800 D**oicesti (OEP800D), belonging to SC OMV Petrom - VI Muntenia Central Production Zone, is located at periphery of Doicesti village, approximately 2 km of DN 71 Targoviste - Sinaia (N: 440 59 '07. 7 ″, E: 250 25' 00. 0 ″, altitude 267 m). It was opened in 1982 and has 685 m² as surface. The activity which is held in the park consists in the collection, storage the oil and salted water mixture produced by 21 oil wells, gravitational separation of the mixture into distinct phases, pumping of crude oil and water to reservoir 1 Aninoasa Park. Specific facilities of technological process and extraction operational flow of crude oil and natural gas in the park are: five reservoirs with 20 m^3 capacity and two reservoirs with 50 m^3 for oil and salted water and a one reservoir with 20 m^3 capacity for freshwater. Also, there are two pumps for oil pumping and two tanks collectors to collect the accidental spillages (4 m^3 and 8 m^3, respectively). The park is located on a hilly area which favoring the extension of pollutions in the case of accidental breakage. During the years there have been many accidental spillages due pipelines breakage from Park 800 Doicesti to Park 1 Aninoasa, as well as the pipelines from oil wells to park, the result being a polluted land with oil products (e.g. vicinity of the Bradului Valley Creek). In the present the company already pays some compensation to owners whose land was affected (4430 m²) and monitors the water quality by sampling and analyses conducted quarterly by the EPA Dambovita.

Oil **E**xtraction **P**ark **35 S**otanga (OEP35S) - is situated in extravilan of Sotanga village, about 3 km of DJ 712 Targoviste - Sotanga road (Fig.1). It was opened in 1988 and has an area of 3738 m². The activity which is held in the park consists in the collection, storage oil and salted water mixture produced by 6 oil wells, gravitational separation of the mixture into distinct phases, pumping of crude oil and water to reservoir 1 Aninoasa Park Specific facilities of technological process and extraction operational flow of crude oil and natural gas in the park are: two reservoirs with 20 m^3 capacity and one reservoirs with 50 m^3 for oil and salted water mixture. Also, there is a pump for oil pumping and a tank collector (i.e. 8 m^3) to collect the accidental spillages. The area where the park is located is a hilly area, predominantly forestry, near being the coal mine Sotanga. During the years there have been many accidental spillage due pipelines breakage from Park 35 Sotanga to Park 35 1 Aninoasa. At this time there are no records concerning some pollution of soils around the Park 35 Sotanga.

Oil **E**xtraction **P**ark **7 G**heboieni (OEP7G) - is situated in extravilan of Tatarani village, about 4 km of DN 72A Targoviste - Campulung road (N: 440 57 '53. 8 ″, E: 250 19'

52. 5 ″, altitude 373 m – Fig 1). It was opened in 1974 and has an area of 13.741 m². The activity held in the park is the collection, storage of oil and water mixture produced by 10 wells, which are pumped to the deposit of Central Park Teis. then the collection of water both in Central Park Teis and Park 1 Sovrom, and finally, after temporary storage in these parks, followed the pumping of them to the Park 74 Sotanga in order to injection in layer. Specific facilities of technological process and extraction operational flow of crude oil and natural gas in the park are: three reservoirs with 20 m^3 capacity and one reservoir of 220 m^3 for oil and salted water mixture, one reservoir of 250 m^3 for salted water and one reservoir of 20 m^3 for fresh water. Also, there are two pumps for oil pumping and one for salted water pumping, a collector tank (8 m^3 capacity) for collection the accidental spillages. The park is located on a hilly area, predominantly forestry, on Tisa Valley Creek. During the years there have been many accidental spillages due pipelines breakage from Park 7 Gheboieni to Central Park Teis. In the present the company pays compensations to owners whose lands were affected (i.e. 70013 m²) and monitors the water quality of Tisa Creek by sampling and analyses conducted quarterly by the EPA Dambovita.

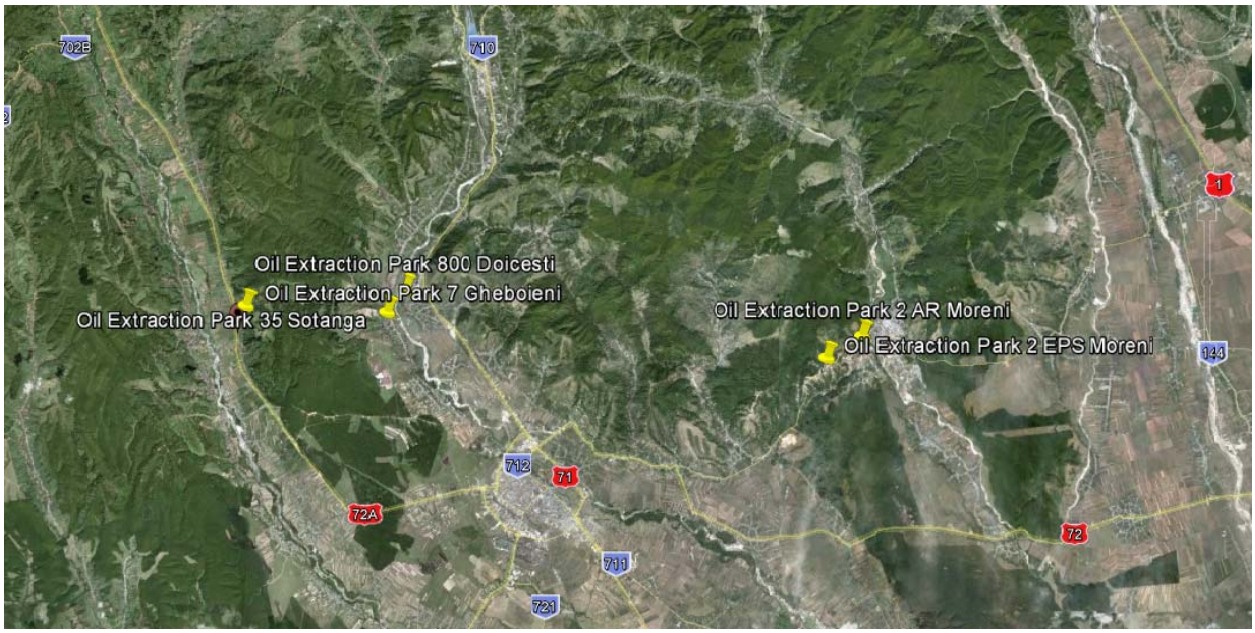

Fig. 1. Investigated areas which are frecventely polluted with crude oil.

Oil **E**xtraction **P**ark **2 AR M**oreni (OEP2ARM) - is located around Moreni city on the road DJ 720 Targoviste - Moreni. It was opened in 1975 and has an area of 4671 m². The activity held in the park consists in collection of fluid extracted through 48 oil wells. gravitational separation of the mixture into distinct phases, temporary storage of separate fluids and pumping of crude oil to South Central Deposit III and a water to injection wells and then to injection station. Specific facilities of technological process and extraction operational flow of crude oil and natural gas in the park are: six reservoirs of 20 m^3, two reservoir of 35 m^3 and three reservoirs of 50 m^3 for oil and salted water mixture, two reservoirs of 200 m^3 for salted water, four reservoirs of 80 m^3 for crude oil and one reservoir of 80 m^3 for fresh water. Also, there are two pumps for oil pumping and two for salted water injection, and two collector tanks (80 m^3 and 100 m^3 capacity) for collection of accidental spillages. This park is wilderness type. During the years there have been many accidental spillages due pipelines breakage from Park 2 AR Moreni to South Central Deposit III.

Oil **E**xtraction **P**ark **2 EPS M**oreni (OEP2EPSM) - is located around Moreni city at 1 km of the road DJ 720 Targoviste - Moreni. It was opened in 1980 and has an area of 9449 m². The activity held in the park consists in collection, storage of crude oil and salted water

mixture, gravitational separation of the mixture into distinct phases, pumping of crude oil and water to South Central Deposit III and a water to injection wells and then to injection station. Specific facilities of technological process and extraction operational flow of crude oil and natural gas in the park are: 24 reservoirs of 20 m^3, two reservoirs of 50 m^3 and two reservoirs of 100 m^3 for crude oil and water mixture, one reservoir of 200 m^3 and one reservoir of 480 m^3 for water, three reservoirs of 250 m^3 for crude oil and one reservoir of for 30 m^3 for fresh water. Also, there are three pumps for oil pumping and one for salted water injection, and one collector tank for accidental spillages. This park is wilderness type being located at South - East of Pascov Creek and North-East of Pascovel Creek. During the years there have been many accidental spillages due pipelines breakage from Park 2 EPS Moreni at South Central Deposit III.

2. MATERIALS AND METHODS

2.1. SAMPLING

The soil samples were collected in November 2011 from five locations of oil extraction areas (i.e. Doicesti, Sotanga, Gheboieni, 2AR Moreni and 2EPS Moreni), owned by SC OMV Petrom, from two depths (0-5 cm and 30 cm) according with data presented in Table 1. The sample points (four sample from each location) was selected by the next criteria: land morphology; flow direction of phreatic; contamination level of edaphic coating. Sampling was achieved from points with crude oil contaminated soil and from points with soil apparently uncontaminated, considered as blanks, as well. Sampling procedure was achieved acoording with Romanian Order 184/1997 and Guidance Document 4-04. *Petroleum Remediation Program (PRP). Soil Sample Collection and Analysis Procedures* by Minnesota Pollution Control Agency [11]. In this respect for each sampling sites (Table 1 and Fig. 1) 25 soil cores were taken to a depth of 0-5 cm and 30 cm at 5 m intervals on a grid measuring 20 m x 20 m around the reservoirs and tanks. This mini-grid approach was chosen in order to minimise the variation at each site. Samples were combined and the resulting composite sample weighed approximately 0.5–1 kg for each selected point from each selected sites. Then the samples were placed in clear polythene bags and transported to laboratory. All soil samples were air-dried at ambient temperature, then were sieved through 1 mm mesh.

2.2. METHODS

After some preliminary analysis of the samples it was carry out some complex analyzes of investigated areas, such as Energy-Dispersive-X-Ray-Fluorescence analysis (EDXRF) [12, 13]. EDXRF analyzes of soil samples (sites no. 1-5) were performed by using ElvaX spectrometer. To check the analytical precision, randomly chosen samples (about 20% of the total numbers) were measured in triplicate according to International Standard Reference Material: NIST SRM 2709, 2710 and 2711 for soil. Average recoveries (n=4) were 84, 72, 79, 89, 102 and 99% for Zn, Cd, Cr, Cu and Pb, respectively.

Measurements of pH values were carried out in deionized water with a soil: water ratio of 1:2 according to the NF ISO 10390/2005 procedure. 10 g of soil samples were mixed with 50 mL 0.1 N KCl solution, for 30 min. under stirring. After one hour, the mixture was filtered and the pH determination was done with Consort P501 pH-meter at room temperature (20.4^0C). The conductivity measurement in saturated solution of soil extract was done by HACH CO150 instrument.

Table 1. The investigated points of oil extraction area.

Oil **E**xtraction **P**ark 800 **D**oicesti (OEP800D)		Coordinate	
Sample	Depth	Latitude	Longitude
OEP800D1	0 – 5 cm	44''59'50.21	25''25'50.22
OEP800D2	30 cm	44''59'50.21	25''25'50.22
OEP800D3	0 – 5 cm	44''59'50.96	25''25''49.77
OEP800D4	30 cm	44''59'50.96	25''25''49.77
OEP800D5	0 – 5 cm	44''59'50.64	25''25'48.94
OEP800D6	30 cm	44''59'50.64	25''25'48.94
OEP800D7	0 – 5 cm	44''59'49.80	25''25'48.84
OEP800D8	30 cm	44''59'49.80	25''25'48.84
Blank1	0 – 5 cm	44''59'50.47	25''25'51.04
Blank2	30 cm	44''59'50.47	25''25'51.04
Oil **E**xtraction **P**ark **35 S**otanga (OEP35S)			
OEP35S1	0 – 5 cm	44''58'55.46	25''22'09.58
OEP35S2	30 cm	44''58'55.46	25''22'09.58
OEP35S3	0 – 5 cm	44''58'54.04	25''22'08.84
OEP35S4	0 – 5 cm	44''58'54.04	25''22'08.84
OEP35S5	30 cm	44''58'53.61	25''22'09.98
OEP35S6	0 – 5 cm	44''58'53.61	25''22'09.98
OEP35S7	30 cm	44''58'55.07	25''22''10.67
OEP35S8	0 – 5 cm	44''58'55.07	25''22''10.67
Blank3	30 cm	44''58'54.51	25''22'12.04
Blank4	0 – 5 cm	44''58'54.51	25''22'12.04
Oil **E**xtraction **P**ark **7 G**heboieni (OEP7G)			
OEP7G1	0 – 5 cm	44''57'53.78	25''19'50.99
OEP7G2	30 cm	44''57'53.78	25''19'50.99
OEP7G3	0 – 5 cm	44''57'52.84	25''19''50.07
OEP7G4	30 cm	44''57'52.84	25''19''50.07
OEP7G5	0 – 5 cm	44''57'53.78	25''19'50.99
OEP7G6	30 cm	44''57'53.78	25''19'50.99
OEP7G7	0 – 5 cm	44''57'52.81	25''19'51.07
OEP7G8	30 cm	44''57'52.81	25''19'51.07
Blank5	0 – 5 cm	44''57'53.09	25''19'52.99
Blank6	30 cm	44''57'53.09	25''19'52.99
Oil **E**xtraction **P**ark **2 AR M**oreni (OEP2ARM)			
OEP2ARM1	0 – 5 cm	44''58'44.27	25''38'14.99
OEP2ARM2	30 cm	44''58'44.27	25''38'14.99
OEP2ARM3	0 – 5 cm	44''58'43.04	25''38'14.89
OEP2ARM4	30 cm	44''58'43.04	25''38'14.89
OEP2ARM5	0 – 5 cm	44''58'42.23	25''38'14.29
OEP2ARM6	30 cm	44''58'42.23	25''38'14.29
OEP2ARM7	0 – 5 cm	44''58'44.28	25''38'13.12
OEP2ARM8	30 cm	44''58'44.28	25''38'13.12
Blank7	0 – 5 cm	44''58'44.79	25''38'14.68
Blank8	30 cm	44''58'44.79	25''38'14.68
Oil **E**xtraction **P**ark 2 EPS Moreni (OEP2EPSM)			
OEP2EPSM1	0 – 5 cm	44''58'26.89	25''37'18.34
OEP2EPSM2	30 cm	44''58'26.89	25''37'18.34
OEP2EPSM3	0 – 5 cm	44''58'28.02	25''37'19.85
OEP2EPSM4	30 cm	44''58'28.02	25''37'19.85
OEP2EPSM5	0 – 5 cm	44''58'27.81	25''37'21.72
OEP2EPSM6	30 cm	44''58'27.81	25''37'21.72
OEP2EPSM7	0 – 5 cm	44''58'26.32	25''37'21.25
OEP2EPSM8	30 cm	44''58'26.32	25''37'21.25
Blank9	0 – 5 cm	44''58'29.73	25''37'26.95
Blank10	30 cm	44''58'29.73	25''37'26.95

3. RESULTS AND DISCUSSION

Usually, the investigations concerning the pollution level of soil with crude oil can be achieved by direct observation (visual) or by analysis of toxic metals according with Romanian legislation, Order 756/1997 respectively. The geological and hydrogeological characteristics of investigated areas are very important for this study because both can amplified or reduced the pollution level of soil or groundwater. The geotechnical studies executed in analyzed areas indicate the presence of edaphic coating over maximum 4 meters and a complex macroporous loess deposits on the next 6-8 m. The groundwater is met from approximately 15-20 m. depending on the investigated area.

Heavy metals concentration, including Cu, Cr, Cd, Zn and Pb, for all 50 contaminated soil samples were centralized in Table 2. These results were compared with the maximum values admitted by the Romanian legislation, according with Order 756/1997 (Table 3).

The EDXRF technique established the following concentration of heavy metals in the investigated contaminated areas:

In the **O**il **E**xtraction **P**ark 800 **D**oicesti (OEP800D) the pH of soil samples was moderate basic with values between 7.69-7.54 and weak basic at 30 cm depth, the values being from 7.23 to 7.43. The soil samples were collected according with Romanian Order 184/1997 and Guidance Document 4-04 of MPCA, depending on oil extraction activities established by owned Company. In this respect the samples were collected from the points around of all seven reservoirs and two collector tanks the range of sampling started from suspected source of pollution, increasing the distances between the collection points to areas presumed to be contaminated, on all cardinal directions taking care that the distances from contaminated sources to be greater on the dominant wind direction but respecting the mini-grid approach. The area where is located the park is a hilly region favoring the expansion of pollution in the case of accidental breakage. Thus can be explained the exceeding over MAL values, according with Romanian legislation (Table 3), for concentrations of Pb at surface and 30 cm depth, as well as for concentration of Cd, Cr and Cu for samples collected at 0-5 cm depth (Table 2). Amount of Zn shown some exceed on reservoirs points (Table 2) comparative with MAL provided by Order 756/1997, the values being on the range of maximum level, between 300-700 mg/kg d.w (Table 3). During the last years it is well known by EPA Romania that in this area were a lot of accidental spillages due pipelines breakage from Park 800 Doicesti to Park 1 Aninoasa, and thus the result was a high pollution of soil with heavy metals as a consequence of crude oil extraction activities.

The pH values in **O**il **E**xtraction **P**ark **35 S**otanga (OEP35S) are on the range 7.98 and 7.61 corresponding to a pH moderate basic at both selected depth (Table 2). All the soil samples were collected in according with Order 187/1997 and Guidance Document 4-04 (MPCA) stated from polluting sources (three reservoirs, one pump and one collector tank) on the dominant wind direction but respecting the mini-grid approach. The OEP35S is a hilly area, predominantly forestry, near to the coal mining Sotanga. The high concentrations of Pb, Cd, Cr, Cd and Zn (Table 2) compared with MAL values accepted by Romanian legislation (Table 3) can be explained by several accidental spillages due to the pipelines breakage from Park 35 Sotanga to Park 1 Aninoasa, as well as the coal mining activities developed in this area.

The pH in **O**il **E**xtraction **P**ark **7 G**heboieni (OEP7G) is moderatly basic on the range 7.51 and 7.99 at both selected depth (Table 2). Considering the crude oil extraction activity developed in this park, the soil samples were achieved according with Order 756/1997 and Guidance Document 4-04 (MPCA) stating from polluted sources (six reservoirs, three pumps and one collector tank) on the dominant wind direction but respecting the mini-grid approach.

Table 2. The pH value, soil reaction and mean concentrations of heavy metals of contaminated samples.

Oil **E**xtraction **P**ark 800 **D**oicesti (OEP800D)		**Heavy metal [mg/kg w.d.]**				
	pH/soil reaction	**Pb**	**Cr**	**Cd**	**Cu**	**Zn**
OEP800D1	7.64/ moderate basic	22.23±1.5	2.66±0.1	2.51±0.2	29.61±2.1	397.1±3.4
OEP800D2	7.43/ weak basic	21.35±2.1	2.19±0.1	2.18±0.3	22.83±3.4	278.3±3.1
OEP800D3	7.73/ moderate basic	20.08±0.8	1.78±0.2	2.19±0.1	21.35±2.9	386.3±2.8
OEP800D4	7.21/ weak basic	20.26±1.2	1.53±0.2	1.92±0.1	20.03±2.4	262.0±2.5
OEP800D5	7.63/ moderate basic	21.34±1.7	2.16±0.1	2.39±0.3	26.66±1.9	358.4±2.5
OEP800D6	7.39/ weak basic	21.10±0.9	1.98±0.3	2.01±0.1	24.78±1.2	279.5±2.9
OEP800D7	7.69/ moderate basic	20.67±0.5	2.33±0.2	2.26±0.4	24.09±1.6	368.9±4.1
OEP800D8	7.23/ weak basic	20.45±1.1	2.28±0.1	1.82±0.2	23.65±2.1	221.0±2.2
Blank1	7.29/weak basic	18.97±0.3	1.59±0.2	1.62±0.1	20.88±1.8	256.8±3.1
Blank2	7.11/neutra – weak basic	18.12±0.5	1.06±0.1	1.28±0.2	20.13±1.7	208.3±3.7
Oil **E**xtraction **P**ark **35 S**otanga (OEP35S)						
OEP35S1	7.98/ moderate basic	24.54±1.7	2.45±0.2	2.84±0.6	32.45±3.1	311.9±4.3
OEP35S2	7.61/ moderate basic	23.98±1.5	2.02±0.2	2.43±0.1	21.37±3.4	253.1±4.7
OEP35S3	7.83/ moderate basic	22.09±2.1	2.21±0.3	2.53±0.4	29.67±2.4	276.3±3.6
OEP35S4	7.61/ moderate basic	21.47±0.9	1.82±0.1	2.19±0.1	21.65±2.6	244.1±3.3
OEP35S5	7.69/ moderate basic	22.87±1.3	2.14±0.5	2.63±0.5	30.45±2.6	252.8±3.5
OEP35S6	7.50/ moderate basic	21.03±1.4	1.62±0.1	1.92±0.3	25.31±2.7	201.4±3.1
OEP35S7	7.82/ moderate basic	22.98±1.5	2.34±0.1	2.41±0.2	33.45±3.3	267.8±3.1
OEP35S8	7.64/ moderate basic	21.05±0.8	1.70±0.2	1.85±0.2	24.89±2.5	213.9±3.6
Blank3	7.26/weak basic	20.41±0.6	1.42±0.1	1.33±0.1	20.98±2.1	189.3±2.6
Blank4	7.21/weak basic	19.13±0.4	1.02±0.1	1.11±0.1	20.11±2.2	166.9±2.6
Oil **E**xtraction **P**ark **7 G**heboieni (OEP7G)						
OEP7G1	7.99 moderate/ basică	21.39±1.2	1.92±0.3	2.61±0.1	28.76±	154.9±
OEP7G2	7.67/ moderate basic	20.67±1.8	1.76±0.1	1.83±0.2	21.09±2.6	133.1±4.5
OEP7G3	7.73/ moderate basic	22.03±2.2	2.18±0.5	2.59±0.3	29.87±2.8	241.3±4.1
OEP7G4	7.51/ moderate basic	21.67±2.5	1.83±0.2	1.95±0.1	20.08±2.4	198.6±3.6
OEP7G5	7.67/ moderate basic	22.56±1.5	2.09±0.3	2.34±0.6	27.43±2.2	201.4±3.2
OEP7G6	7.49/ weak basică	21.45±1.1	1.65±0.1	1.82±0.2	20.92±2.6	166.3±3.4
OEP7G7	7.88/ moderate basic	23.98±1.4	2.29±0.4	2.73±0.5	28.65±2.5	209.3±3.2
OEP7G8	7.62 moderate basic	22.87±0.7	1.74±0.2	2.04±0.2	21.23±2.6	154.1±3.1
Blank5	7.25/weak basic	20.67±0.3	1.42±0.1	1.65±0.1	21.09±2.2	133.2±3.5
Blank6	7.29/weak basic	19.34±0.4	1.18±0.1	1.21±0.1	20.66±2.1	116.7±3.4
Oil **E**xtraction **P**ark **2 AR M**oreni (OEP2ARM)						
OEP2ARM1	7.98/ moderate basic	23.76±1.6	2.63±0.3	2.82±0.4	38.72±4.1	265.4±3.8
OEP2ARM2	7.69/ moderate basic	21.84±1.3	2.01±0.4	2.31±0.1	29.34±2.2	199.3±2.4
OEP2ARM3	8.01/ moderate basic	23.19±1.9	2.31±0.4	2.74±0.5	37.32±3.2	293.1±4.6
OEP2ARM4	7.66/ moderate basic	22.76±2.2	1.84±0.5	2.03±0.2	28.45±2.8	204.6±3.1
OEP2ARM5	7.89/ moderate basic	23.10±1.5	2.11±0.6	2.68±0.2	37.88±2.3	256.1±4.6
OEP2ARM6	7.25/ weak basic	22.46±1.3	1.67±0.1	1.94±0.1	29.45±2.7	177.2±2.4
OEP2ARM7	7.88/ moderate basic	23.51±1.1	2.03±0.3	2.73±0.4	36.12±3.1	232.9±3.8
OEP2ARM8	7.55/ weak basic	21.60±1.2	1.43±0.3	1.84±0.3	28.77±2.6	155.3±2.8
Blank7	7.33/ weak basic	20.39±0.6	1.29±0.1	1.47±0.1	22.35±2.7	160.2±3.1
Blank8	7.18/ weak basic	19.47±0.3	1.02±0.1	1.21±0.2	20.88±2.4	128.1±3.2
Oil **E**xtraction **P**ark 2 EPS **M**oreni (OEP2EPSM)						
OEP2EPSM1	7.97/ moderate basic	23.41±1.8	2.68±0.4	2.87±0.3	36.57±2.9	304.2±3.7
OEP2EPSM2	7.62/ moderate basic	21.33±1.4	1.87±0.2	2.11±0.1	29.54±3.2	241.5±3.3
OEP2EPSM3	7.89/ moderate basic	23.22±1.2	2.49±0.5	2.74±0.6	39.54±3.1	276.4±3.9
OEP2EPSM4	7.63/ moderate basic	21.41±1.9	1.72±0.1	2.09±0.2	29.11±3.6	220.1±2.6
OEP2EPSM5	8.09/ moderate basic	23.24±2.2	2.61±0.4	2.79±0.1	38.02±2.8	269.4±4.6
OEP2EPSM6	7.61/ moderate basic	21.37±2.7	1.84±0.2	2.03±0.3	29.11±2.5	213.6±4.4
OEP2EPSM7	8.04/ moderate basic	23.51±1.2	2.34±0.4	2.83±0.3	39.34±3.1	286.3±3.6
OEP2EPSM8	7.63/ moderate basic	22.24±1.5	1.94±0.3	2.12±0.4	30.23±3.3	219.2±3.1
OEP2EPSM1	7.29/weak basic	20.44±1.0	1.52±0.1	1.52±0.1	23.45±2.7	256.7±2.5
OEP2EPSM2	7.11/ weak basic	19.51±0.4	1.13±0.1	1.22±0.2	21.92±2.5	189.4±2.4

Table 3. Maximum admitted level (MAL) of heavy metals in soil according with Order 756/1997 from Romanian legislation.

Reference values of heavy metals [mg/kg d.w.]			
Metals	Normal level	Maximum level	Intervention level
Cadmium (Cd)	1	3-5	5-10
Copper (Cu)	20	100-250	200-500
Manganese (Mn)	900	1500-2000	2500-4000
Nickel (Ni)	20	75-200	150-500
Lead (Pb)	20	50-250	100-1000
Zinc (Zn)	100	300-700	600-1500
Chromium (Cr)	1	4-10	10-20
Iron (Fe)	3000	3000-4500	4500-7000

The Oil Extraction Park 7 Gheboieni is located on a hilly area, predominantly forestry, on Tisa Creek Valley, and in the last years many accidentally spillages (e.g. pipelines breakage) was conducted to a high pollution of soil, surface water and groundwater as well. From this point of view the high concentrations on Pb, Cd, Cu, Cr and Zn were founded on the analyzed soil samples (Table 2) comparative with the MAL values specified in Romanian legislation (Table 3).

The pH of soils in **O**il **E**xtraction **P**ark **2 AR M**oreni (OEP2ARM) is range from 7.55 and 8.01, on the both depths, with a moderately basic reaction of soil. In this park, a complex activity is developed by the 48 oil well where the crude oil is extracted, collected, separated, stored and finally pumped to South Central Deposit III of the SC OMV Petrom Company. The soil samples were collected according with Order 756/1997 and Guidance Document 4-04 (MPCA) stating from polluted sources (seventeen reservoirs, four pumps and two collector tanks) on the dominant wind direction but respecting the mini-grid approach. The park is located on a wilderness area, and many accidental spillages, due pipelines breakage from Park 2 AR Moreni to South Central Deposit III, were over the years. Higher amounts on Pb, Cd, Cu, Cr and Zn on soil samples (Table 2) comparative with the MAL values specified in Romanian legislation (Table 3) were founded by using EDXRF technique.

The pH of soil in **O**il **E**xtraction **P**ark **2 EPS M**oreni (OEP2EPSM) is range from 7.63 to 8.09, on the both depths, with a moderately basic reaction of soil. The activity developed in this park is complex as well. The same activities such as extraction, collection, separation, storage and finally the pumping of crude oil to the South Central Deposit III are developed by SC OMV Petrom Company. Also, in this case high concentrations on Pb, Cd, Cu, Cr and Zn were founded on the analyzed soil samples (Table 2) comparative with the MAL values specified in Romanian legislation (Table 3).

All blank samples collected from the five oil contamined sites had a neutral to weak alkaline pH and the values of heavy metals contrations, including Pb, Cr, Cd, Cu and Zn were framed in MAL values according with Order 756/1997 from Romanian Regulation.

Solubility of heavy metals in soil is strongly dependent on the soil acidity. Thus, the soil pH is determined by the nature of the soil, biological and chemical processes that occur into the soil, vegetation, fertilizers used, mineral and organic acids, carbon dioxide which results in soil through respiration of plants, animals and decomposition of inorganic substances from microorganisms, etc. Physical activity, chemical and biological of soil is influenced by maintaining an active concentration of hydrogen ions in soil solutions. In the analyzed cases, when crude oil extraction activity is combined with coal mining activity (i.e. Sotanga coal mine) or with industrial activity (i.e. Moreni parks) certainly increase both the pH of soils from acid to alkaline values and the organic content of the soil as well.

In all contamined soil samples was founded a higher concentration of lead, on the both depths. It is well known that lead as a toxic metal gets unto soil through crude oil extraction activities, as well as through dry and wet depositions from the atmosphere and other mining or industrial effluents and solid discharges near to the selected oil extraction parks. Lead exhibits long residence time, sparingly soluble as a result of rapid conversion to $Pb(SO_4)$ at the soil surface and it forms relatively stables organo-metal complexes or chelates with organic matter of soil. In soil with pH of more than 5.0 (acid) to 7.5-8.0 (moderate basic) and at least 5% organic matter, atmospheric Pb is retained in the upper 2 to 5 cm of undisturbed soil but when exist some crude oil spillages then the lead is present at more 40 cm depth. In the same time these lead species are strongly sorbed to Fe/Mn oxides, and in this case can be more important than association with clays and organic matter. The sorption process of lead onto Fe/Mn oxides is not affected by aging but is dependent by pH of soil.

The higher concentration of copper in analyzed soil samples can be explained by that the copper has a high affinity for clay mineral fractions, especially those rich in coatings containing organic carbon and manganese oxides (e.g. Sotanga mine) and as a result, residues are often elevated in sediments near localized sources of inputs.

The higher amount of cadmium in soil samples can be interpreted by the retention process of the metal in carbonates, which explains its greater mobility and its availability to plants. It is well known that zinc is a metal which can be damaged for soil when its concentration increase over the admitted value, and then easy can be mobilized in soil especially under metallic (oxy) hydroxides. Cadmium and zinc, closely link to carbonates are sensitive to pH changes and they can be mobilized when the pH becomes acid.

These metals associations with oxides and organic fractions are not dangerous for the environment, but when the environment becomes increasingly reducing or oxidizing depend to pH of soil heavy metals can be mobilized and can increase the hazard level.

4. CONCLUSIONS

Crude oil extraction activity brings serious heavy metal contamination of soil. The heavy metals accumulation in the soil is due to various factors such as: the nature of soils, the relief, and the litology, the hydrology, the climate, the dominant winds, the soil reaction, the cathionic exchange capacity, the use of the land, and not least the source of contamination, which is various depending by oil extraction, coal mining, industrial and anthrophic activities developed on the selected five parks (Doicesti, Sotanga, Gheboieni, 2AR Moreni and 2 EPS Moreni). The risk associated with the presence of metals in soil depends by their ability to transfer in water or plants. The higher concentrations of Pb, Cd, Cu, Cr and Zn were found in all contaminated soil samples (Table 2), more exceeding the MAL values specified in Romanian legislation. According with these data, each metal can cause pollution of soil with dangerous implication concerning the environment and health.

REFERENCES

[1] Dulama, I.D.., Popescu, I.V., Stihi, C., Radulescu, C., Cimpoca, Gh.V., Toma, L.G., Stirbescu, R., Nitescu, O., *Romanian Report on Physics*, **64**(4), 2012.

[2] Popescu I.V., Frontasyeva M., Stihi C., Cimpoca Gh.V., Radulescu C., State G., Gheboianu A., Oros C., Cilicov, O., Bancuta, I., Dulama, I.D, *Romanian Reports on Physics,* **63**, 1205, 2011.

[3] Stihi, C., Radulescu, C., Busuioc, G., Popescu, I.V., Gheboianu, A., Ene, A., *Romanian Journal of Physics*, **56**(1-2), 257, 2011.

[4] State, G., Popescu, Ion V., Gheboianu, A., Radulescu, C., Dulama, I., Bancuta, I., Stirbescu, R., *Romanian Journal of Physics*, **56**(1-2), 2011.

[5] Popescu, I.V., Frontasyeva, Stihi, C., Cimpoca, Gh.V., Radulescu C., Gheboianu, A., Oros, C., Vlaicu, Gh., Petre, C., Bancuta, I., Dulama I.D., *Romanian Journal of Physics*, **55**(7-8), 8212010.

[6] Radulescu, C., Stihi, C., Busuioc, G., Gheboianu, A.I., Popescu, I.V., *Bull. Environ. Contam. Toxocol.,* **84**(5), 641, 2010.

[7] Radulescu Cristiana, Stihi, C., Busuioc, G., Gheboianu, A.I., Popescu, I.V., Cimpoca, V.Gh., *Romanian Biotechnological Letters*, **15**(4), 5444-5456, 2010.

[8] Stihi, C., Busuioc, G., Radulescu, C., Elekes, C.C., Ciulei, C., *Bulletin UASVM Agriculture*, **68**(2), 143, 2011.

[9] Radulescu, C., Stihi, C., Popescu, I.V., Nitescu, V.O., Gheboianu, A.I., Cimpoca, Gh.V., Dulama, I.D., Chilian, A., Bucurica, A., Bancuta, O.R., *Journal of Science and Arts,* **15**(2), 193, 2011.

[10] Radulescu, C., Stihi, C., Popescu, I.V., Busuioc, G., Gheboianu, A.I., Cimpoca, Gh.V., Dulama, I.D., Diaconescu, M., *Ovidius University Annals of Chemistry*, **21**(1), 9, 2010.

[11] ***** Guidance Document 4-04. *Petroleum Remediation Program (PRP). Soil Sample Collection and Analysis Procedures* by Minnesota Pollution Control Agency (MPCA)

[12] Radulescu, C., Stihi, C., *Metode analitice complementare pentru determinarea concentratiei de metale grele*, Editura Bibliotheca, Târgovişte, 2011.

[13] Popescu, I.V., Radulescu, C., Stihi, C., Cimpoca, Gh.V., Dulama, I.D., *Tehnici analitice utilizate in studiul poluarii mediului,* Editura Bibliotheca, Târgovişte, 2011.