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Effects of metals from oil to polluted soil

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Abstract: Oil pollution of extraction areas is an undesirable phenomenon, but very present, especially in old farms. In the context in which the depollution of these areas, in Romania, is carried out from public funds, this fact is more and more difficult to achieve. That is why the effect of pollutants on the environment is being analyzed more and more, it often remains that the depollution is done naturally. This material analyzes the effect of metals present in crude oil (Cu, Pb, Zn, Ag, Ni, Mn, As, Cd, V, Cr, S), on the soil affected by a historical accidental pollution in the Moinesti area, Romania. This article presents the results of analyzes performed by metal detection techniques, namely optical emission spectrophotometry with inductive coupled plasma and atomic absorption spectrophotometry. The metals determined in the polluted soil were statistically analyzed regarding the dispersion, standard deviation and coefficient of variation compared to the control sample and compared with the results from two areas in Romania. The risk of exploitation of polluted areas was also analyzed, namely the method of pollution indices and the method of combining the effects of pollutants.

Keywords: metals, oil, pollution, soil.

1. Introduction

Crude oil is defined as a solution consisting of hydrocarbons, metals, non-metals, water [1].

If we were to fully analyze the crude oil extracted from all areas of the earth, we would probably determine more than half of the elements of the periodic table, with concentrations ranging from high percentages of carbon and hydrogen and low percentages of nitrogen and sulfur. Transitional metals would also be determined.

Metal constituents were identified in crude oil (Na, Li, Be, Mg, Ca, Ba, Sr, Cu, Ag, Zn, Cd, Se, Y, La, B, Al, Si, Sn, Pb, Cr, Mo, W, Fe, Co, Ni, Ti, V, Mn), the most abundant being nickel and vanadium [2,3].

Metal constituents are in different percentages in different areas of exploitation around the world, but may differ in the same deposit (Table 1).

Metals can provide information on crude oil migration and its age [4].

T.F.Yen was able to show that the metals in crude oil can be grouped into petroporphyrins and neporphyrins. Thus, five classes were determined, namely [5]:

- metalloporphyrin chelates (V, Ni),
- complex metal complexes, small tetradentate ligands (V, Ni, Fe, Cu, Cr, Co),
- carboxylic acid salts of the functional polar groups of resins (Mo, Zn, Ge),
- colloidal minerals (silica and NaCl),
- organometallic compounds (Hg, Sb, As).

Porphyrins are the first compounds isolated from crude oil that have demonstrated the organic nature of crude oil.

Porphyrin is a macrocyclic system consisting of four pyrrole rings linked by four methine groups, being a class of nitrogen-derived macrocycles. Porphyrins can accept two hydrogen ions to form a diacid with +2 charge or they can give up two protons to become a -2 anion with charge. This characteristic of porphyrins leads to the formation of organo-metallic complexes with a structure similar to hemoglobin in the blood and that of chlorophyll in green plants. Porphyrins in crude oil demonstrate its formation at low temperatures from organic matter (at high temperatures, porphyrins decompose) [6].

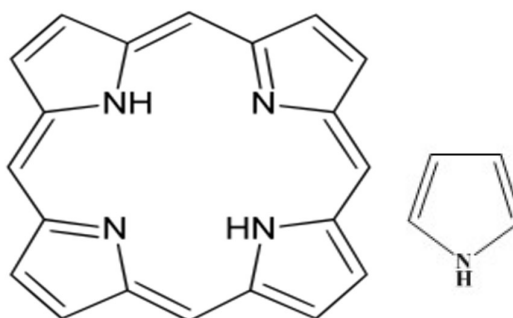


Figure 1. The structure of porphyrin and the pyrrole group [6].

Non-porphyrins in crude oil include other ring systems such as strongly substituted porphyrins. Porphyrins with UV properties other than those mentioned above and porphyrin decomposition products is detected in oil samples [7].

Asphaltenes have bound in their composition metals such as vanadium, nickel and iron which vary in amounts from 5 ppm to several thousand. Asphalt metals are partially bound in porphyrins, which are an integral part of them [8].

Table 1. Concentration of metals ($\mu\text{g} / \text{g}$) in crude oil from various regions [9]

Elements	California, USA	Lybia	Alberta, Canada
Na	13.3	13.0	3.62
Ni	98.4	49.1	9.38
Cu	0.93	0.19	0
Fe	68.9	4.94	10.8
Mn	1.20	0.79	0.01
Zn	9.76	62.9	0.046
Cd	0.004	0	0

2. Materials and Methods

2.1. Geology of structures

The analyzed area is placed in Moinesti city, parts of bacau Conty, Romania. Area is parts of the External Unit of the Eastern Carpathian Flysch, being constituted by three folds oriented north-south, with faulted flanks.

The deposits that make up the analyzed structure belong to the Eocene, Oligocene and Miocene [10].

The Eocene appears in the facies of the Bisericani (Church) Layers, being made up of black and green shale marls, micaceous, slightly sandy.

The Oligocene develops under the characteristic facies known in the External Unit of the flysch, being composed of the following horizons:

1. the horizon of the Lucăcești sandstone - with a thickness of about 10 - 15 m, made up of a sandstone complex,
2. the horizon of white bituminous marls, up to 150 m thick,
3. the horizon of the disodils and lower menilites, with a thickness of about 50 m, consisting of bituminous clay rocks and weak intercalations of Kliwa sandstones,
4. the horizon of Kliwa sandstone, with a thickness of about 350 m, consisting of alternations of banks with siliceous sandstones and packages with disodiles ,
5. the Suprakliwa horizon with a thickness of about 59 - 112 m, made up of alternations of Kliwa tiles with disodiles ,
6. the horizon of the disodils and upper menilites, consisting of disodilic schists, with intercalations of menilites and intercalations of Kliwa sandstone ,

The Transition horizon, with a thickness between 22 and 46 m, formed by intercalations of microconglomerates, siliceous sandstones, clays and disodiles .

The Miocene consists of blackish compact clays and marls, with intercalations of compact sandstones and salt.

The oil area deposits consists mainly of siliceous sandstones with a higher clay content, so that the flow properties are slightly diminished by the horizons of the Suprakliwa and Kliwa sandstones which have an insignificant volume of clay.

The extraction of crude oil took place between 1960-2000, after which it was abandoned.

No soil decontamination was performed because the concentration in petroleum substances was below the intervention threshold, ie below 1000 mg / kg dry matter (the land being a less sensitive area).

The oil extraction and treatment facilities were removed and the land was cultivated with flowers (marigolds).

Soil samples were collected using geological probes at a depth of 100 mm from 12 places located in an oil extraction and treatment area.

The treatment of the soil samples taken in order to perform the analyzes was performed according to the standard SR ISO 11464/1998 - Soil quality.

Pretreatment of samples for physico-chemical analyzes. Thus, the samples were oven dried and crushed with an electric soil mill.

2.2. Atomic absorption spectrophotometry

The determinations were performed using a Shi-madzu AA-6300 double beam spectrophotometer (Shimadzu Corporation, Japan).

It is equipped with: ASC-6100F autosampler, flame atomizer and graphite furnace, deuterium lamp for background correction and cavity cathode lamps for the studied elements.

The method SR ISO 8288: 2001 was used to determine copper and zinc. SR EN 14083: 2003 and SR EN ISO 15586: 2004 methods were used to determine cadmium and lead, with modifications to suit the type of matrix analyzed.

Each determination was performed in three repetitions.

For the calibration, 5 concentrations of the reference solutions were used, the correlation coefficients of the calibration rights being in the range 0.9780-0.9997.

To evaluate the degree of recovery of heavy metals from the analyzed soils, a series of samples were created with solutions of known concentrations of these metals, the recorded recovery degrees being: 91.14% for Cd, over 93.52% for Pb, 94.92% for Cu and 95.02% for Zn.

2.3. Inductively coupled plasma optical emission spectrophotometry

Initial determinations of macro and microelements were made by inductively coupled plasma optical emission spectrometry using a Perkin Elmer Op-tima 5300 DV spectrometer.

The wavelengths used for each element are the following: Ca - 315,887 nm, Cu - 327,393 nm, Cr - 267,716 nm, Mn - 257,610 nm, Ni - 231,604 nm, Pb -217.00 nm and Zn - 206,200 nm.

2.4. Analysis of experimental data

Atomic absorption spectrophotometer control, data acquisition and analysis.

Primary spectral data was performed using WizAard (Shimadzu Corporation, Japan).

The quantitative data matrix was processed in Microsoft Excel (Microsoft) for statistical calculations (arithmetic mean calculation, standard deviation, Pearson correlation coefficient).

The Pearson coefficient was used to characterize the correlations between the measured contaminant concentrations.

2.5. Analysis of the environment polluted with metals

The exploitation of crude oil is a set of operations that can lead to soil and ground-water pollution.

The interest of researchers to study the risk of environmental pollutants is well known, the research works being focused on determining the hydrocarbon content in soil and plants and less on those dedicated to qualitative and quantitative analysis of soil and plant metal content [11, 12].

The studies focused on the development of a model for assessing the risk of pollutants determined from oil, for certain study areas.

A model for assessing the risk in exploitation of the land affected by pollution, on the Bayesian model was developed by Aguilera [13] and developed by Diana Mariana Cocârță [14].

An analysis of a land, which must be returned to use after the completion of onshore operations includes in addition to determining the content of petroleum products and determining 14 elements of the periodic table, namely Cu, Pb, Zn, Ag, Ni, Mn, As, Cd, V, Cr and S [15] (figure 2 and table 2).

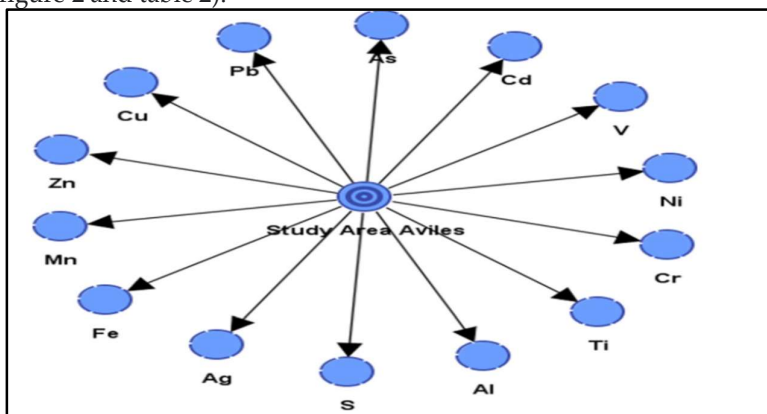


Figure 2. Impact assessment of the main metals in oil polluted areas [15].

An analysis of the effects of metals found in soils in areas where there have been oil mines, was performed by A. R. Karbassi [16,17,18]:

After a pollution, the analyzes must indicate if there are traces of petroleum product (THP), radioactive elements and especially metals.

For the analysis of the environmental impact of metal pollution from the exploitation of oil fields, a variant of risk composition based on Bayesian networks is proposed [19], starting from the relation:

$$P(x) = P(X_1, X_2, X_3, \dots, X_n) = \prod_{i=1}^n P\left(\frac{X_i}{X_{j(i)}}\right), \quad (1)$$

Where $X_{j(i)}$ are data taken from the acyclic graph of the variables X_i .

Table 2. Concentration of approved metals in soil pollution (mg / kg dry matter) [21,22,23,24]

Metals	Normal values	Threshold sensitive area alert/less sensitive	Intervention threshold sensitive areas/less sensitive
Cu (mg/kg)	20	100-250	200-500
Pb (mg/kg)	20	50-250	100-1000
Zn (mg/kg)	100	300-700	600-1500
Ag (mg/kg)	2	10-20	20-40
Ni (mg/kg)	20	75-200	150-500
Mn (mg/kg)	900	1500-2000	2500-4000
As (mg/kg)	5	15-25	25-50
Cd (mg/kg)	1	3-5	5-10
V (mg/kg)	50	100-200	200-400
Cr (mg/kg)	30	100-300	300-600
S (mg/kg)	-	400-5000	1000-20000

Muller designed a pollution index also called Igeo [25] and defined by the equation:

$$geo = \log_2 \frac{C_n}{1.5 \cdot B_n}, \quad (2)$$

Where:

C_n is the metal concentration measured in the sample collected,

B_n – metal concentration as reference,

1,5 – a calculation factor,.

Another model for determining pollution classes was described by Enrich-ment [26] in relation to:

$$EF = \frac{\left(\frac{C_n}{C_{Mn}}\right)_{analysis\ sample}}{\left(\frac{C_n}{C_{Mn}}\right)_{sample\ analysis-soil\ not\ pollution}}, \quad (3)$$

C_{Mn} is the concentration of manganese in the soil sample taken,

Tables 3 and 4 show the pollution classes for the two mathematical models presented above.

Table 3. Pollution classes according to the Igeo index [27]

Igeo Index	Pollution type
Igeo ≤ 0	Reduced pollution
Igeo = 0-1	Normal values
Igeo = 1-2	Sensitive area alert threshold
Igeo = 2-3	Less sensitive area alert threshold
Igeo = 3-4	Intervention threshold sensitive area
Igeo = 4-5	Intervention threshold less sensitive area
Igeo ≥ 5	Extreme pollution

Another method of determining ecological risk measurement levels is re-presented by the relationships between the ecological risk description and the risk index [28,29].

$$EE_r^i = T_r^i \cdot \frac{C_i}{C_0}, \tag{4}$$

$$RI = \sum_{i=1}^n T_r^i \cdot \frac{C_i}{C_0}, \tag{5}$$

C_i is the metal concentration in the analyzed sample,
 C_0 – the metal concentration in the control sample,
 T_r^i – toxicity factor,(toxicity factor is $As = 10, Cu = Pb = Ni = 5, Zn = Mn = 1, Cr = 2$),
 E_r^i it is the ecological risk factor,
 RI represents the risk index of the presence of metals in the soil.

Table 4. Pollutin classes accordin to the Enrichment index - EF [27]

Level EF	Pollution level
EF ≤0	Reduced pollution
EF =0-1	Normal values
EF =1-2	Sensitive area alesrt threshold
EF =2-3	Less sensitive area alert threshold
EF =3-4	Intervention threshold sensitive area
EF =4-5	Intervention threshold less sensitive area
EF ≥5	Extreme pollution

The pollution classes used in the method of determining the levels of ecological risk measurement are expressed in Table 5.

Table 5. Pollutin classes accordin to the ER and RI index [30,31,32]

Level ER	Value ER	Risk	Level RI	Risk
0	<40	Reduced	<110	Reduced
1	40-80	Moderate	110-200	Moderate
2	80-160	Considerable	200-400	Considerable
3	160-320	Big	>400	Big
4	>320	Catastrophic		

3. Results

In order to analyze the pollution status of a land, we took samples from an area where there were oil exploitations, the results being presented in table 6 and figure 3.

Table 6. Soil sample position

Nr. crt.	Measurement point
1.	Parking lot
2.	Vertical tank 250 mc,
3.	Buried tank
4.	Vertical tank 200 m³, salt water
5.	Vertical tank 20 m³, oil and water
6.	Vertical tank 20 m³, oil and water
7.	Oil, gas and water pipelines keyboard
8.	Vertical separator oil, water, gas 3,85 m3 - 8 bar
9.	Vertical separator oil, water, gas
10.	Vertical separator oil, water, gas 3,85 m3 - 8 bar
11.	Vertical separator oil, water, gas
12.	Oil, gas and water pipelines keyboard

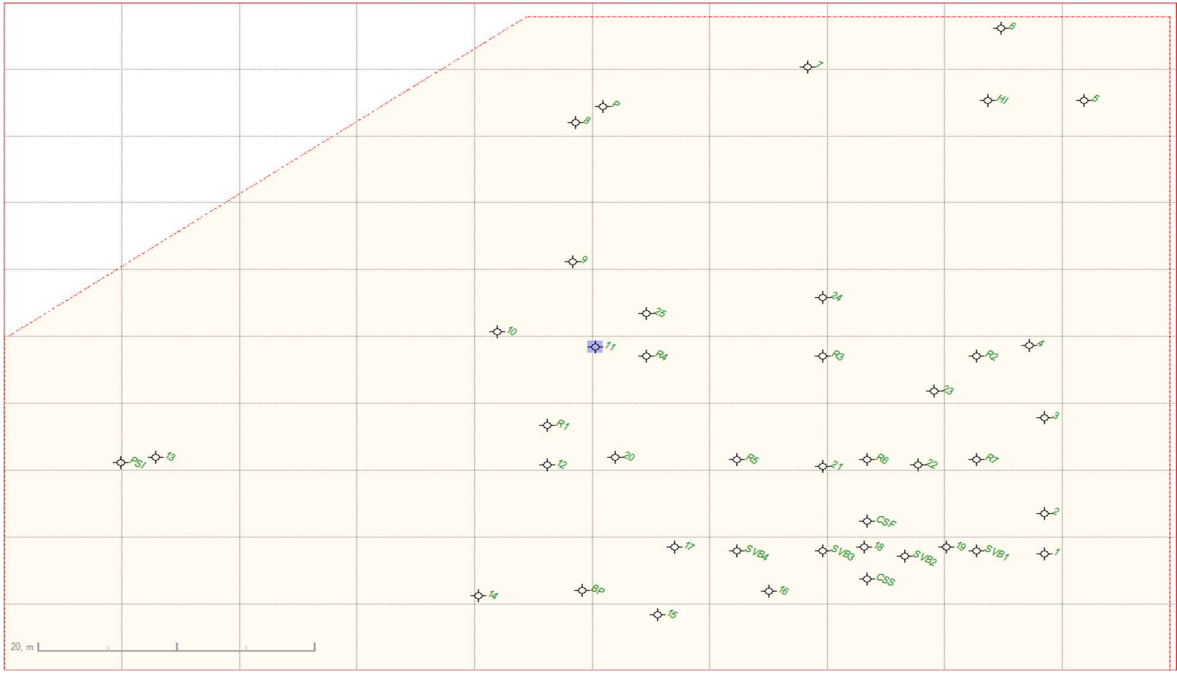


Figure 3. ketch of the analysis area with the presentation of the measurement and sampling points

Table 6. Metal content in the analyzed area (Moinești) (mg/kg)

Location	Pb	Ni	V	Cd	Zn	Ag	Cu
1	20	170	120	0,60	170	1,8	150
2	17	150	100	0,50	200	2,0	190
3	23	190	150	0,80	268	1,7	180
4	27	195	190	0,50	240	2,2	120
5	16	120	200	1,05	115	3,6	200
6	23	130	180	0,44	110	3,5	198
7	25	140	185	0,38	450	2,2	159
8	25	160	150	0,48	328	4,9	190
9	23	190	195	0,25	338	3,9	199
10	21	180	178	0,95	125	2,8	197
11	81	162	146	0,58	700	2,7	192
12	35	190	188	0,65	265	2,9	188
Min	16	120	100	0,38	110	1,7	120
Max	81	195	195	0,65	700	4,9	200
Mediate	28	164,75	165,17	0,60	275,75	2,85	18,25
Dispersion	590,17	2782,89	2673,53	0,08	51781,85	1,46	3620,68
Standard deviation	24,29	52,75	51,70	0,27	227,55	1,21	60,17
Coefficient of variation	0,97	0,26	0,34	0,69	2,54	0,80	0,37
Control sample value	25	200	150	0,40	90	1,5	160
Cluj Value	0,8	10	70	0,005	4,21	0,01	0,75

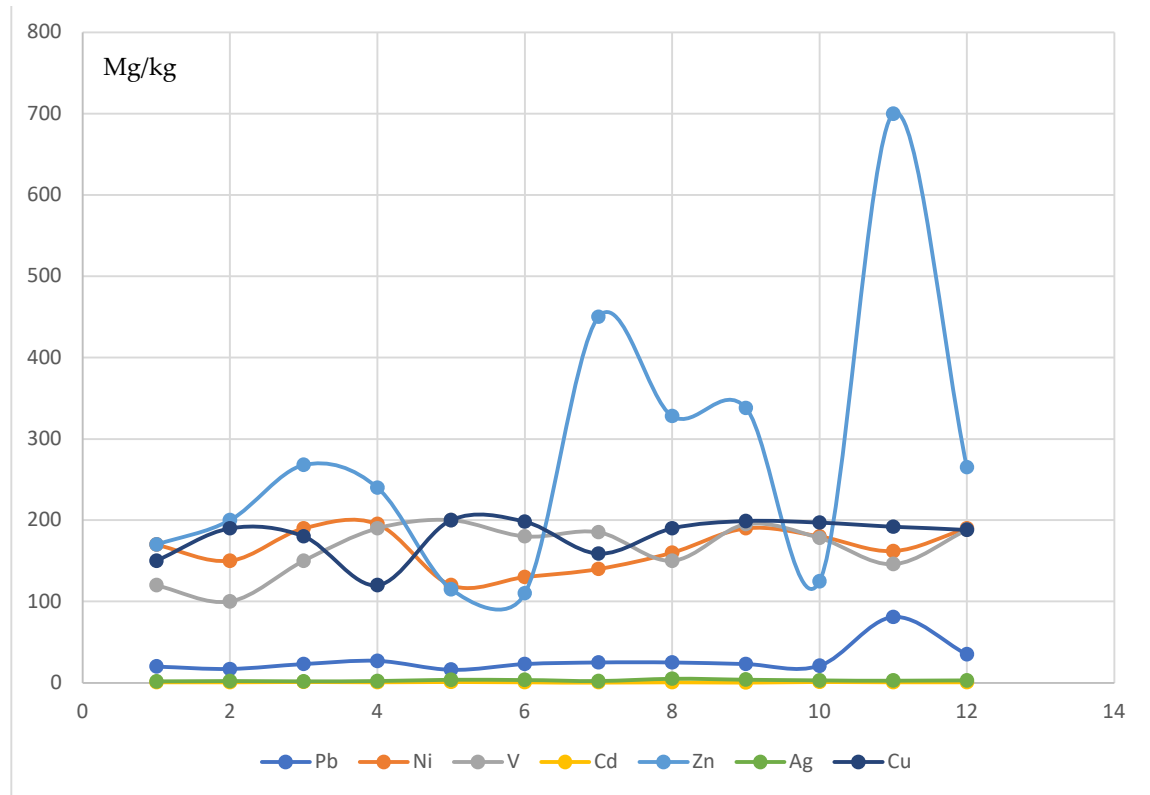


Figure 4. Metals contents in soil sample

The results of applying the method based on the Igeo pollution index (relation 2), respectively the ecological risk and the risk index (relations 4.5) are explained in tables 7 and 8.

Table 7. Pollution index to Pb, Ni, V

Locațion	Pb	Igeo	EE	Ni	Igeo	EE	V	Igeo	EE
1	20,00	- 0,91	4,00	170,00	- 0,82	4,25	120,00	- 0,91	4,00
2	17,00	- 1,14	3,40	150,00	- 1,00	3,75	100,00	- 1,17	3,33
3	23,00	-0,71	4,60	190,00	- 0,66	4,75	150,00	- 0,58	5,00
4	27,00	- 0,47	5,40	195,00	- 0,62	4,88	90,00	- 0,24	6,33
5	16,00	- 1,23	3,20	120,00	- 1,32	3,00	200,00	- 0,17	6,67
6	23,00	- 0,71	4,60	130,00	- 1,21	3,25	180,00	- 0,32	6,00
7	25,00	- 0,58	5,00	140,00	-1,10	3,50	185,00	- 0,28	6,17
8	25,00	- 0,58	5,00	160,00	- 0,91	4,00	150,00	- 0,58	5,00
9	23,00	- 0,71	4,60	190,00	- 0,66	4,75	195,00	- 0,21	6,50
10	21,00	- 0,84	4,20	180,00	- 0,74	4,50	178,00	- 0,34	5,93
11	81,00	1,11	16,20	162,00	- 0,89	4,05	146,00	- 0,62	4,87
12	35,00	- 0,10	7,00	190,00	-0,66	4,75	188,00	- 0,26	6,27
Control sample value	25,00			200,00			150,00		
RI			67,20			49,43			66,07

Table 8. Pollution index to Cd si Zn

LocaŃion	Cd	Igeo	EE	Zn	Igeo	EE
1	0,60	- 0,00	7,50	170,00	0,33	9,44
2	0,50	- 0,26	6,25	200,00	0,57	11,11
3	0,80	- 0,42	10,00	268,00	0,99	14,89
4	0,50	- 0,26	6,25	240,00	0,83	13,33
5	1,05	0,81	13,13	115,00	- 0,23	6,39
6	0,44	- 0,45	5,50	110,00	- 0,30	6,11
7	0,38	- 0,66	4,75	450,00	1,74	25,00
8	0,48	- 0,32	6,00	328,00	1,28	18,22
9	0,25	- 1,26	3,13	338,00	1,32	18,78
10	0,95	0,66	11,88	125,00	-0,11	6,94
11	0,58	- 0,05	7,25	700,00	2,37	38,89
12	0,65	0,12	8,13	265,00	0,97	14,72
Control sample value	0,40			90,00		
RI			89,75			183,83

Table 9. Pollution index to pentru Ag si Cu

LocaŃie	Ag	Igeo	EE	Cu	Igeo	EE
1	1,80	-0,32	6	150	-0,67	4,68
2	2,00	-0,16	6,66	190	-0,33	5,93
3	1,70	-0,40	5,66	180	-0,41	5,62
4	2,20	-0,03	7,33	120	-1	3,75
5	3,60	0,67	12	200	-0,26	6,25
6	3,50	0,63	11,66	198	-0,27	6,18
7	2,20	-0,03	7,33	159	-0,59	4,96
8	4,90	1,12	16,33	190	-0,33	5,93
9	3,90	0,79	13	199	-0,27	6,21
10	2,80	0,31	9,33	197	-0,28	6,15
11	2,70	0,26	9	192	-0,32	6
12	2,90	0,36	9,66	188	-0,35	5,87
Control sample value	1,50			160		
RI			114			67,59

4. Discussion

Oil exploration can also create accidental pollution with heavy metals.

Even if the concentration of total hydrocarbons in the soil is within the limits that do not require intervention for depollution, rather high concentrations of metals have been determined.

The analyzes found that the metals were adsorbed by the soil (through plants) and in the control sample area collected from more than 1 km away from the crude oil exploitation area.

Crude oil extraction areas are usually located at fairly large distances from human settlements, but the presence of metals in the soil can lead to their leaching in transitional waters (groundwater).

Also, in the analyzed plants, metal concentrations were discovered, which makes it necessary to determine the metallic elements in the case of the analysis of an oil exploitation area, under ecological reconstruction.

The plants, as seen especially in the control sample, take the metals from the air, being transferred to the soil.

For the treatment of the soil, in the analyzed area marigolds and lettuce were used as crops.

It is recommended not to use these vegetable products.

5. Conclusions

It is observed that the pollution with metals, coming from crude oil, is present in the extraction area, being over 10 times bigger than a residential area.

All samples collected have determined values of the amount of metals within the control limits.

Depollution intervention is not recommended, but it is recommended to maintain agricultural crops that naturally treat the removal of metals.

Lead pollution is present especially in the area of the biphasic separator, where the elimination of gases in the atmosphere, due to the opening of the safety valve and the non-tightening of the valves created the possibility to remove metals in the exhaust gases

It's an alert threshold.

Zinc pollution is present in areas where gas leaks have occurred, the area being at moderate risk in operation.

As can be seen, metal pollution is only monitored in three cases, with the amounts of metals in the soil showing close values in the test sample.

Also, the analysis of the risk in operation by the two methods is very useful, the results being similar comparative.

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Conflicts of Interest: “The authors declare no conflict of interest.”.

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