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## Assessment of soil quality in an area with hydrocarbon exploitation activities

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# Assessment of soil quality in an area with hydrocarbon exploitation activities

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**Abstract.** The paper presents an analysis of the soil quality, in the petroleum field from Independenta, Galati. The study was determined by the fact that the hydrocarbon spills from the activity carried out here can have a significant impact on the environment. The paper presents the determinations carried out on soil samples related to heavy metal content and pH. Samples were taken from different areas, starting from a contaminated source, and continuing with the surroundings. For each area, three samples were taken at different levels of depth. Concentration values were compared with the legislation [1] setting out the procedures and technical rules for identifying environmental damage in order to determine the responsibilities for remedying them.

## 1. Introduction

Soil is the loose, soft, and brittle layer at the surface of the earth's crust, which, together with the surrounding atmosphere, constitutes the plant life [2]. Soil quality studies have the role of controlling the situation in a targeted zone, bearing in mind that there is a hydrocarbon exploitation activity in the area. The surveyed area for soil quality tracking is located on the territory of Galați County, approximately 22 km away from Galati city, to the NW cardinal directions. It is an area where oil extraction activities take place and therefore, in the pursuit of the evolution of soil quality monitoring, it was taken into account that the hydrocarbon leakage and the atmospheric emissions from the activity carried out here can have a significant impact over the environment.

For quantitative assessment of soil pollution level, samples were taken from a potentially contaminated area within the oil extraction wells. At the same time, samples were taken from several areas surrounding to the oil wells in order to be compared with each other. The investigated perimeter covers a large area, that extend up to an agriculture field, due to the dispersive character of the exploited hydrocarbons. Agricultural works can be carried out because the active probes occupy relatively small areas and are connected to the reservoir park via access roads, electricity networks, and the transport pipelines of the mixture.

The criteria that were taken into account when setting the soil sampling points were: the assessment of contaminated soil composition from a near place of an oil well, and the comparison of the results with other neighbouring areas, such as: the edge of oil well zone, soil cultivated with wheat, and uncultivated soil from nearby.

The four areas selected for sampling are distributed as follows: zone 1 (S1), located inside the square, approximately 3 m from the oil well; zone 2 (S2), located outside the square, approximately 20 m from the oil well, with uncultivated soil; area 3 (S3), wheat-cultivated soil, located approximately



40 m from the probe; area 4 (S4), with uncultivated soil surrounding a tree, located about 30 m from the well.

The three soil samples, were taken at different depths, as follows: S 1.1, S 2.1, S 3.1, S 4.1 - 15 cm deep; S 1.2, S 2.2, S 3.2, S 4.2 - depth 30 cm; S 1.3, S 2.3, S 3.3, S 4.3 - depth 45 cm.

The samples were transported and analysed in the Stationary Laboratory for Soil Analysis at the Galati Engineering Faculty where the following indicators were determined: pH and heavy metals (titanium, manganese, iron, zinc, lead, rubidium, strontium, zirconium, chromium, arsenic, cobalt, copper and nickel).

## 2. Methods to analyze the heavy metals concentration

Heavy metals are metals with a density greater than 5 kg/dm<sup>3</sup>. They are generally toxic, especially their residues which cause environmental pollution. Heavy metals can reach within the soil from the other environmental factors, air and water. These pollutants migrate in depth through complex diffusion, adsorption, dissolution, having water as solvent. In the soil, a number of microorganisms can solubilize the heavy metals, causing imbalances in physical, chemical and biological processes.

For analysis, the soil samples were first dried in a thermo-regulable oven for 24 hours at 105°C. This is necessary to remove the water molecules, physically bound to the soil. Of all 12 samples, about 5 grams were collected, which, after being finely ground, were placed in plastic envelopes. Quantitative analysis was performed using the X-ray spectrophotometer.



**Figure 1.** Soil preparation for the determination of the heavy metal concentration.

The values of the analytical determinations for the soil samples taken within the analyzed perimeter were compared with the reference values according to the national regulations, namely the MAPPM Order no. 756/1997 [3].

## 3. Results and discussion

### 3.1 Determination of heavy metals

Table 1 shows the normal values, the alert threshold, and the intervention threshold for land in the use category, depending on the sampling site. For samples in zone 1, alert thresholds and intervention thresholds are used for comparison, for the Lesser Sensitive land (for industrial use). In the case of samples taken from areas 2, 3 and 4, outside the square, the alert or intervention threshold values for land in the Sensitive usable area (agricultural use of the surrounding land), are used for comparison [4].

Analysing zone 1, it is found that samples S 1.1 and S 1.2, taken from the depths of 15 cm and 30 cm respectively, contain besides other metals (titanium, manganese, iron, zinc, lead, etc.), the nickel metal, which was not found in sample S 1.3, or in the other areas. Moreover, the nickel concentration exceeds the normal value, but not the threshold of alert. Another aspect is the lead, which in sample S 1.2, is found in a low concentration, below the measuring limit of the measuring device. Also, other heavy metals such as titanium, iron, zirconium and nickel, which are found in higher concentrations in S 1.2, are found, while manganese, is found to be smaller in comparison with the other samples. Also

in sample S 1.2, we identify arsenic, which is in a concentration higher than the normal value, but it does not exceed the threshold of alert, imposed by the regulation, being also a metal rarely encountered in the area. It should also be noted that the concentration level decreases with the depth, to zirconium and rubidium, while at strontium, it increases.

**Table 1.** Reference values (mg/kg) according to MAPPM Order no. 756/1997.

Traces of elements	Normal values	Thresholds of alerts		Thresholds of intervention	
		Types of use		Types of use	
		Sensitive	Less sensitive	Sensitive	Less sensitive
Arsen	5	15	25	25	50
Cobalt	15	30	100	50	250
Chromium	30	100	300	300	600
Copper	20	100	250	200	500
Manganese	900	1500	2000	2500	4000
Nickel	20	75	200	150	500
Lead	20	50	250	100	1000
Zinc	100	300	700	600	1500

Note: In the table, are noted only the metals found in the samples.

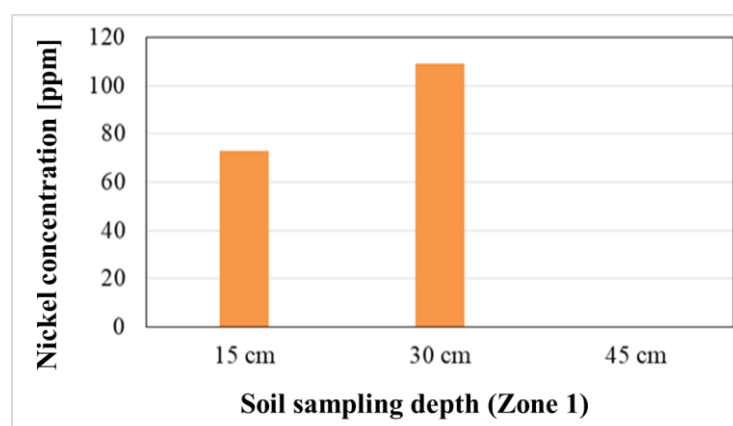
**Table 2.** The content of metals, and their concentration, in zone 1.

Metal	S <sub>1.1</sub>	Error	S <sub>1.2</sub>	Error	S <sub>1.3</sub>	Error
Ti	4654	532	5177	529	4396	535
Mn	494	56	356	52	544	57
Fe	28196	540	28420	549	26729	513
Zn	55	7	50	7	47	7
Pb	18	5	12		24	5
Rb	94	4	92	4	90	4
Sr	94	4	99	4	111	4
Zr	310	8	336	8	310	8
Cr						
As			20	5		
Co						
Cu						
Ni	73	24	109	25		

Note: The concentration is expressed in ppm.

In zone 1, samples S 1.1 and S 1.2 were found to be nickel, metal not found in the other samples taken. The level of nickel concentration exceeds the registered normal value, by almost 5 times, but does not reach the statutory threshold, because it is considered a "less sensitive" area (industrial use). We must remember that the area has been contaminated with petroleum products (salt water and petroleum), which can determine the presence of the metal [5].

Zone 2, located at the edge of the square, is about 20 m from the oil well, and is not cultivable because agricultural machinery does not penetrate so close, leaving a free space between the oil extraction perimeter and the cultivated land. In this area, various plant species are grown, such as wormwood (*Artemisia absinthium*) and several types of burdocks (*Lappa major*, *Lappa minor* and *Lappa tomentosa*).



**Figure 2.** Level of nickel concentration in zone 1.

**Table 3.** Results recorded in zone 2.

Metal	S <sub>2.1</sub>	Error	S <sub>2.2</sub>	Error	S <sub>2.3</sub>	Error
Ti	5046	533	4883	530	4252	513
Mn	579	59	560	58	513	56
Fe	28490	550	28308	540	28292	542
Zn	57	8	60	8	84	9
Pb	26	5	20	5	21	5
Rb	92	4	90	4	85	4
Sr	97	4	90	4	98	4
Zr	313	8	309	8	305	8
Cr						
As						
Co						
Cu						
Ni						

Note: The concentration is expressed in ppm.

The results recorded in zone 2 show that for many of the metals (titanium, manganese, iron, rubidium, zirconium) the concentration decreases with depth. Zinc concentration, increases with depth. Lead and strontium have roughly equal values in each of the three samples, but in sample S 2.2, we identify copper, a rare metal found in the area, taking into account, the 12 samples that were taken for analysis.

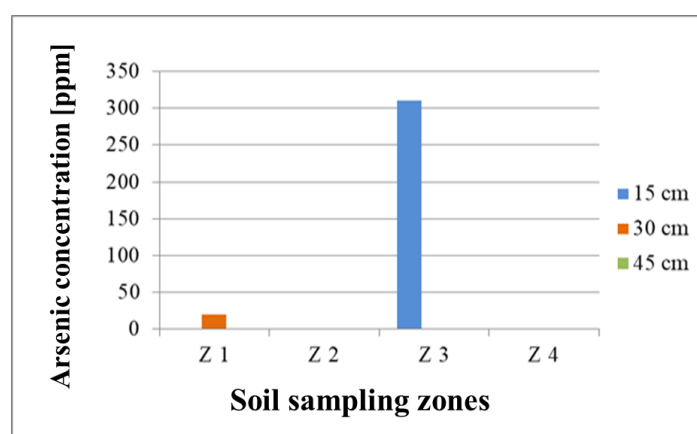
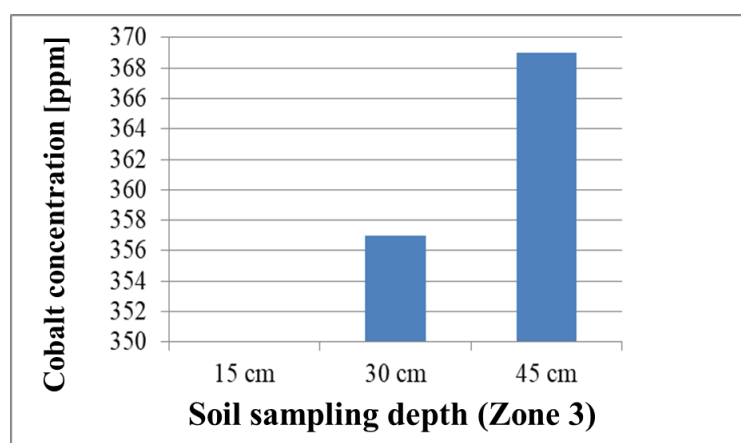
Analysing the results in zone 3, we find that titanium, iron, zinc and lead have a decreased concentration level in sample S 3.2, but return, in sample S 3.3, to the initial form in S 3.1. Strontium and zirconium, after maintaining the same level, in the first two samples, drop in the last sample. The arsenic identified in the first sample has fairly high values, higher than the intervention threshold. The same applies to cobalt, identified in samples S 3.2 and S 3.3, which exceeds the intervention threshold imposed by the regulation.

In area 3, where the field is cultivated with wheat, sample S 3.1 indicates very high arsenic values, exceeding not only the normal value, but also the alert and intervention thresholds for soils of the "sensitive" category. A comparison was made, with this category of use, because that the soil sample was extracted from the outside of the probe square, so a land of agricultural use. The value of exceeding the alert threshold is more than 20 times, and the intervention threshold, is more than 12 times. These results show that the amount of arsenic in the soil is very high. Because of this, we must track, the source from which the metal comes from.

**Table 4.** Concentration of the metals in zone 3.

Metal	S <sub>3.1</sub>	Error	S <sub>3.2</sub>	Error	S <sub>3.3</sub>	Error
Ti	5118	536	4763	511	5257	519
Mn	700	63	618	59	553	57
Fe	28761	555	27496	527	28801	547
Zn	78	8	46	7	68	8
Pb	24	5	23	5	20	5
Rb	106	4	98	4	101	4
Sr	99	4	99	4	90	4
Zr	326	8	326	8	281	7
Cr						
As	310	4				
Co			357	117	369	119
Cu						
Ni						

Note: The concentration is expressed in ppm.

**Figure 3.** The concentration of arsenic in the 4 zones.**Figure 4.** The value of the cobalt concentration in zone 3.

In the zone 3, where the land is cultivated with wheat, sample S 3.1 indicates very high arsenic values, exceeding not only the normal value, but also the alert and intervention thresholds for soils of the "sensitive" category. Overruns were 12 times above the alert threshold, and more than 7 times

above the intervention threshold, which, gives a lot of attention to the state of the soil and the environment in general.

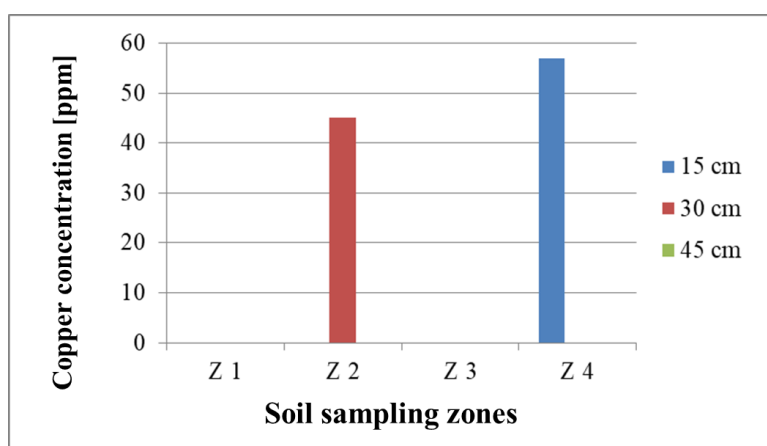
Zone 4 is located about 30 m from the probe, in an uncultivated area, due to a tree, around 15 m<sup>2</sup> of unused agricultural land. As in area 2, where the soil, is not cultivated, there are many plant species specific to the area, such as wormwood (*Artemisia absinthium*), *Cerotocarpus arenarius*, burdock (*Lappa major*, *Lappa minor* and *Lappa tomentosa*), etc. Because around this tree, the land is cultivated, there is the possibility that the soil is affected by the fact that in the agricultural activity, a series of compounds are used to control pests, stimulate growth etc.

**Table 5.** Concentration of the metals, in zone 4.

Metal	S 4.1	Error	S 4.2	Error	S 4.3	Error
Ti	4964	534	4894	531	5466	546
Mn	665	63	707	63	537	59
Fe	28871	565	28389	548	29098	564
Zn	56	8	65	8	62	8
Pb	25	5	19	5	26	5
Rb	98	4	98	4	92	4
Sr	98	4	96	4	104	4
Zr	325	8	325	8	337	9
Cr					208	64
As						
Co						
Cu	57	13				
Ni						

Note: The concentration is expressed in ppm.

Analysing how metals are distributed in zone 4, we find that the only metals that exceed normal, but not the alert threshold values, are copper and chromium but each of them is found only in one of the samples (see Table 5). The other materials behave as in the previous cases, stagnate, and then grow or decrease as a level of concentration, or show fluctuations.



**Figure 5.** The level of copper concentration in the 4 zones.

Copper, identified in samples S 2.2 at a depth of 30 cm and S 4.1 at a depth of 45 cm, exceeds the normal value imposed by the regulations in force but does not reach the alert threshold in any of the two areas where it was identified

### 3.2 Determination of pH in soil samples

Soil pH is a very important element that needs to be known and supervised because it intervenes in many physicochemical and biological soil mechanisms. Determination of pH is made either in a soil suspension in water or in a soil suspension in hydrochloric acid solution, with the indication that the latter is less than that in the aqueous suspension, with about 0.5 units. Because the soil contains water, it has been divided according to the pH value into three major categories: acid, neutral and alkaline. As for organic matter, we will not encounter soils with pH in one extreme or another, unless there are strong sources of pollution. Generally, the soil has a pH between 4 and 8 units. The pH ranges from 0 to 14. Between 0 and 7, the pH is acidic, 7 is neutral and between 7 and 14 is alkaline. Most cultivated plants prefer neutral and slightly acidic soils [6].



**Figure 6.** Soil preparation for pH determination.

The pH value, determined in aqueous soil suspension, is an easy to obtain analytical index, based on which the soil reaction and the acid-base properties of the soil-water system are characterized. The soil is first dried, then weighed in parts of 20 grams.

The weighed sample is introduced in a 100-150 ml beaker of KCl or distilled water. The contents were stirred for about 2 minutes and left for a slow decantation for 5 minutes. After the reading electrode is completely inserted into the solution for about 1 minute, the pH value was read, which corresponds to the acidity of the soil sample being researched.

**Table 6.** Determination of soil pH in the 12 samples taken.

<b>Zone 1</b>	<b>pH</b>	<b>Depth (cm)</b>
S <sub>1.1</sub>	7.7	15
S <sub>1.2</sub>	6.72	30
S <sub>1.3</sub>	6.44	45
<b>Zone 2</b>	<b>pH</b>	<b>Depth (cm)</b>
S <sub>2.1</sub>	7.73	15
S <sub>2.2</sub>	7.25	30
S <sub>2.3</sub>	7.24	45
<b>Zone 3</b>	<b>pH</b>	<b>Depth (cm)</b>
S <sub>3.1</sub>	8.14	15
S <sub>3.2</sub>	7.39	30
S <sub>3.3</sub>	7.31	45
<b>Zone 4</b>	<b>pH</b>	<b>Depth (cm)</b>
S <sub>4.1</sub>	7.79	15
S <sub>4.2</sub>	7.53	30
S <sub>4.3</sub>	7.16	45



Analysing each area, we find that only samples S 1.2 and S 1.3 in zone 1 are recorded values below 7 (neutral), is slightly acidic. The other samples taken from the four areas are slightly alkaline, with values close to the neutral zone. This indicates that the pH of the soil is almost ideal for plant growth. The only sample with an index of more than 8 units is located in zone 3, where the field is cultivated with wheat, and it is possible that the pH value is influenced by the treatment applied to the crop.

After determining the pH in the soil, we find that the measured values of the measurements are within the normal limits, close to the neutral zone.

#### 4. Conclusions

The results obtained from soil sampling were compared with Order 756/1997 for the approval of the Environmental Pollution Assessment Regulation, which sets out the procedures and technical norms for the identification of environmental damage in order to determine the responsibilities for remedying them.

Following the determinations, it has been found that with regard to the pH, the recorded values of the measurements are within the normal limits close to the neutral zone.

With regard to heavy metals, they require increased attention, as some of these metals have far exceeded the alarm threshold, some even the intervention threshold. Heavy metals are compounds that cannot be degraded naturally, have a long retention time in the environment, and in the long run are dangerous because they can accumulate in the food chain. The heavy metals can come from stationary and mobile sources as: fuel burning processes, road traffic. Heavy metals can cause muscular and digestive disorders, can influence plant development, preventing photosynthesis.

In conclusion, further analysis is needed to identify the sources of pollution, which may be the extraction of hydrocarbons or the treatment applied to crops.

#### 5. References

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