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Aspects Pertaining to the Pollution of the Soil by Hydrocarbons and Salt Water

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Abstract

The present paper gives an analysis of certain chemical properties that are characteristic of the superficial areas of a contaminated soil that has been polluted over time with the specific fluids of an oil field. The examined polluted areas had not been, up to the time of research, subjected to any decontamination processes.
The aim of this research is to establish whether an ecological rehabilitation of the land is possible in order to reconnect it to the agricultural chain.

Key words: *contamination, salt water, soluble salts, soil, hydrocarbons*

Introduction

The environmental problems caused by the pollution of the soil and groundwater with hydrocarbons and/or other field fluids have exacerbated in recent years due to the fact that the degree of pollution is affecting more and more residents of the areas in question, on the one hand, and the relevant legislation is becoming increasingly pragmatic and restrictive, on the other hand [1, 2].

It is worth mentioning that in Romania there is a particular characteristic pertaining to the pollution of the soil and groundwater with deposit fluids because the industrial process of oil exploitation has a history of over 100 years. The onset of this industrial activity occurred in the subcarpathian hills of Muntenia. The area in question is located in the region adjacent to a creek that flows through the district.

Oil extraction operations usually go hand in hand with harmful effects on the soil, subsoil and aquifer [3].

Large quantities of formation water having a high content of NaCl (greater than 1188 mg/l) also reach the surface upon oil extraction [6].

The degree of soil pollution with formation water depends on:

- accidentally spilled water amount;
- soil contact duration;
- soluble salt content;
- soil type;

- soil pollutant mass diffusion speed.

Mechanisms of ion exchange or adsorption occur once the salt water impacts the solid layer of the soil, by which chemical elements of saline water are adsorbed into the colloidal complex of the soil.

Maximum soluble salt accumulation depth is variable and is determined by:

- time elapsed from the pollution occurrence, which affects soil pollutant migration and accumulation;
- permeability degree of the different soil layers;
- varying soluble salt concentration in water;
- area pluvial rate.

Soil fertility is affected by oil and formation water as follows:
A ratio of:

- 2% oil products polluting the soil leads to the suppression of seed germination;
- 1% oil products polluting the soil does not have such a massive effect on the agricultural production of the contaminated areas, this tolerance being also dependent on the nature of the cultivated plants.

On-the-spot research of the areas affected by this type of pollution has led to the following findings:

- a segregation of the oil products occurs after the penetration of the soil: low viscosity components reach deeper into the soil, while heavier fraction ones remain in the top soil layers;
- soils which have undergone formation-water pollution form a yellowish-grey soluble salt crust after the production of ion exchange mechanisms and soil drying;
- on flat fields, salt water puddles in low pressure areas, then it evaporates or seeps but the salt remains and gets accumulated over time. Even in the case of persistent puddles, soil salinization occurs without anaerobic processes, akin to natural salinization methods, but the source of the salts remains on the surface;
- on sloping grounds, the water follows the lowest altitudes, ultimately reaching the water courses.

As a result of losses, salt water seeps at different speeds depending on soil texture, an intense salinization being observed hereby showcasing the gravity of the pollution processes. Even in the case of moderate pollution a prolonged draining of salts from the soil is required.

Oil and salt water spills are usually found together in a given area. The pollution with both contaminants is more serious, their cumulative effects being difficult to remove.

In the case of pollution due to highly salted water, the following observations must be taken into account:

- sodium chloride has a toxic effect on plants because of the osmotic absorption of water. It also damages the soil because of Na ion absorption and the elimination of the Ca and Mg ions by the clay and humus particles;
- the concentrations of soluble salts and implicitly of interchangeable sodium hampers the draining from the soil layers bound to be improved;
- salinity has a noticeable effect on the degradation reduction of oil, this degradation being about two times lower in soils of mixed pollution as compared to the ones polluted solely with oil.

Analysis of oil pollution in the surface soil to establish the consequences:

- Hydrocarbons, because their negative immiscibility with water, form an oily coating;

- the oily coating acts upon the fauna and flora;
- hydrocarbons act bacteriostatically, being slightly bacteriostatic because of their low solubility in water;
- some bacteria adapt to the presence of hydrocarbons, metabolizing them.

Once underground, hydrocarbons undergo significant chemical transformations [1]. Both aerobic as well as anaerobic conditions are met in the soil. The rate of oil product degradation in the soil is dependent on the concentration of oxygen in the soil, or, in other words, on the degree of aeration of the polluted soil. Oxidation begins with the formation of peroxides, primary alcohols and mono-carboxylic acids. The final stage of degradation is represented by the formation of carbon dioxide, water and cellular micro-organism material [4]. Biodegradation is accelerated in the presence of certain substances called nutrients (compounds of phosphorus, potassium, nitrogen), of humidity and of a relatively constant temperature, factors leading to a rapid increase in bacteria numbers.

Furthermore, intermediate products with high solubility in water or high volatility may result because of degradation, leading to the expanding of the pollution with increased speed.

Experimental Part

Investigated area of 20,000 m^2 is situated on the banks of a creek in Dâmboviţa.

Sampling programs for the carrying out of soil investigations have been implemented, the results pinpointing the contamination substance. Samples were taken from 11 locations in the contaminated area.

Table 1 presents the locations where samples were taken.

Table 1. Area of sampling

No	Sample code	Area of sampling
1.	A	Soil samples taken from the stream area, 3 m beam pipe on the right bank
2.	B	Soil samples taken from the stream area, 3 m beam pipe on the left bank
3.	C	Soil samples taken from the stream area, 10 m pipe on the left bank
4.	D	Soil samples taken from the stream area to 13 m from the shore pipe right
5.	E	Soil samples taken from Area Para 3 m of the shore pipe right
6.	F	Soil samples taken from the stream area, 3 m pipe on the left bank
7.	G	Soil samples taken from the stream area, 25 m from the well on left bank
8.	H	Soil samples taken from the stream area, 52 m from the well on shore right
9.	I	Soil samples taken from the stream area at 78 m from the well on shore right
10.	J	Soil samples taken from the stream area, 58 m from the well on left bank

Soil pollution is influenced by its physical characteristics. Therefore, were made:

1. Physico - chemical soil to establish indicators stipulated in Order 756/1997 related to the type of pollutant (THP - total petroleum hydrocarbons); Physical analysis method - Chemical analysis indicator used (THP - total petroleum hydrocarbons) is: EN 61010-1-93.

The experimental research was carried out in specialized and approved laboratories. The results obtained are shown in Table 2.

Table 2. Results of experimental samples analyzed

No	Sample code	Depth, cm	Value THP determined, mg/kg dry matter
1.	A	5	8.680
2.	B	5	36.000
3.	C	5	14.920
4.	D	5	10.100
5.	E	5	40.400
6.	F	5	5.600
7.	G	5	23.200
8.	H	5	8.150
9.	I	5	9.040
10.	J	5	14.300

2. The physico - chemical soil for determining fertility, morphologic characteristics, aspects and principles related to improving the soil fertility (pH-soluble salts, chloride ions, sodium ions). They have been subjected to the following tests:
- pH ascertaining via potentiometric method;
- Cl ion ascertaining via Mohr's method;
- Na ion content ascertaining via Mohr's method;
- soluble salt ascertaining via water extraction method 1:5.

The results are listed in Table 3.

Table 3. The results of physico-chemical indicators

Sample code	Depth, cm	pH	Soluble salts %	Cl^- mg/100mg soil	Na^+ mg/100mg soil
A	0-20	7.20	0.22	47.8	29.3
B	0-20	7.40	0.10	21.2	13.6
C	0-20	7.62	0.10	40.7	16.6
D	0-20	8.20	0.29	88.5	41.3
E	0-20	7.80	0.16	35.1	25.1
F	0-20	7.44	0.92	192.9	66.2
G	0-20	7.48	0.75	336.3	63.8
H	0-20	7.19	0.31	83.2	32.87
I	0-20	6.72	0.08	23.0	17.6
J	0-20	7.81	1.16	507.9	110.3

Rules on soil pollution in Order 756/1997 refers both to use sensitive and less sensitive to the land, identified as follows:

- Sensible use is the use of land for residential and recreational areas, for agricultural, sanitary protected areas or areas;
- Less sensitive land use including all existing commercial and industrial uses, and area of land for such uses.

According to the Order no.756 / 1997 are defined:

- Intervention thresholds represent the maximum allowable concentrations for pollutants exceedances provided by regulations.
- Alert thresholds, representing 70% of the intervention thresholds of the same pollutants, PA = 0.7 PI.

Concentrations determined for soil samples collected were compared with thresholds of alert and intervention for sensitive land use. In Table 4 are shown the alert and intervention thresholds.

Table 4. Thresholds alert / intervention

Pollutant	**Normal values**	**Alert Thresholds Types of use**		**Intervention Thresholds Types of use**	
		Sensitive	Less sensitive	Sensitive	Less sensitive
THP Total Petroleum Hydrocarbons	< 100	200	1000	500	2000

The investigated study area is in the vicinity of the stream, so that the area of land use was assigned sensitive.

The determined concentrations for the extracted soil samples were compared to the interpretation limits of the assessed properties, in accordance with the legislation in force [5].

As far as the results are concerned, one can observe that the properties of the soil have been altered, its productive capacity being significantly reduced due to salt water and THP.

In the case of soluble salts, in salinization is very strong evidence J, F and G strong, moderate and weak D and H, the samples A, B, C and E. Sample I is the only one that shows no pollution soluble salts. The presence of soluble salts causes increase extracellular osmotic pressure in the soil, increasing the intracellular her on the plant, so the plants can not absorb water from the soil.

The content of chloride ions is very strong evidence to J, G strong evidence, moderate samples D, F and H. Samples A, B, C, E and I are weakly contaminated with chloride ions. Content of sodium ions is very strong in samples A, D, E, F, G, H and J, strong and moderate C and B. THP indicator recorded exceedances of intervention (significant pollution) than the maximum admissible concentration values imposed as follows: for: A sample of 17.3 times, 72 times the sample B, sample C of 29.8 times, sample D 20 2 times, sample E of 80.8 times, 11.2 times the sample F, sample G of 46.4 times, 16.3 times the sample H, I test 18 times and 28.6 times J.

Conclusions

The chemical properties of the soil are affected by the pollution resulting from accidental pipe spills or discharges of the production chain. The high content of water salts discharged into the soil makes the affected soil highly salinized, resulting in the disappearance of cultivated plants or to drastic production shortcomings.

Salt water pollution, revolving around pipes and oil exploitations, varies depending on the amount of water and according to the duration of the discharge.

The lack of specific devices positioned along the pipes in order to prevent accidental water indrafts and the necessity to dump the entire pipe in the field so that repairs or a possible replacing may occur makes it so that the pollution manifests on much larger surfaces and with greater intensity.

Investigated qualitatively ground the soil samples and the different indicators were analyzed: total hydrocarbons, pH, soluble salts, chlorides, Na cations present pollution chemistry, industrial or indirectly with salt water and oil as follows:

1. Soil pollution is a chemical pollution with minerals - salts and organic substances, petroleum hydrocarbons.
2. Function of soil pollution generating activity stream area is industrial pollution.
3. After the effect that it can cause pollution in the area is an indirect pollution, soil infiltration hydrocarbon and saltwater.
4. Pollutants soil in the area are accidental spills of saltwater and crude oil pipelines crossing the site analyzed

The content of salts in the soil produces the following unfavourable effects upon plant growth:

- When wet, the soil transforms into a muddy, sticky, and water and air tight mass;
- When dry, the soil forms a dry crust that cracks and forms large and hardened clumps;
- The water ingression is hampered by the hydraulic conductivity;
- The water is retained with strong forces, altering the plants' root system;
- The plants record a decreased growth rate, leading all the way to the complete halting of plant growth;
- Soil microbiological activity decreases;
- Soil decalcification and organic matter loss occur.

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Aspecte privind poluarea solului cu hidrocarburi şi apă sărată

Rezumat

In lucrare este prezentată o analiză a unor proprietăţi chimice ale zonelor superficiale ale unui sol poluat în timp cu fluidele caracteristice unui zăcământ de petrol. Zonele poluate studiate nu au fost, până la momentul cercetării, supuse nici unui procedeu de decontaminare. Scopul acestei cercetări este stabilirea posibilităţii reabilitării ecologice a terenului, pentru redarea acestuia circuitului agricol.