THEORETICAL CONSIDERATIONS IN THE SELECTION OF THE OPTIMAL TECHNOLOGY FOR THE DEPOLLUTION OF A CONTAMINATED SOIL WITH LIQUID PETROLEUM PRODUCTS

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Abstract: *Soil pollution with liquid petroleum products is a category of frequently encountered incidents with significant environmental and economic consequences. In most cases of soil pollution, negative effects extend shortly from production to both the subsoil and the atmosphere by evaporation of high volatility pollutant compounds. The problem of soil depollution is, in these circumstances, one of the most complex activities in the field of environmental protection, both theoretically, economically and organizationally.*

Through this paper we aim to show that the correct choice of an efficient depollution technology for a contaminated soil with liquid petroleum products is a very difficult decision especially because of the very large number of variables and interactions on which the final results depend. Soil structure in correlation with the physico-chemical characteristics of the pollutant form specific systems that require specific approaches in the choice of appropriate depollution technologies.

Keywords: *contaminated soil, depollution technologies, liquid petroleum products.*

1. INTRODUCTION

Problems of environmental pollution by oil products has recently become more and more relevant, due to the high cost of work during the use of mechanical, physical, chemical and thermal methods of depollution, as well as their limited capabilities [3, 8]. Soil pollution with liquid petroleum products is a category of frequently encountered incidents with significant environmental and economic consequences. In most cases of pollution of soils with liquid petroleum products, the negative effects expand, shortly after production, both on the subsoil, to the groundwater, through infiltration, and on the atmosphere by evaporation of highly volatile pollutant compounds.

The polluted surface with oil products, as an expression of anthropogenic pressure [2, 3], is like a mosaic in the perimeter of the wells extraction and sometimes outside of them, near oil and gas production refineries or facilities, along the transport pipelines, in the warehouses and refineries, in the car maintenance and washing workshops etc.

The large number of factors influencing the pollution and depollution processes, and the inappropriate way they are addressed, lead to situations where the expected results from the depollution are not achieved. The systematic and organized approach to optimal depollution technology is a prerequisite for achieving favorable results [3].

Through this paper we aim to show that the correct choice of an efficient depollution technology for a contaminated soil with liquid petroleum products is a very important and difficult decision, the equivalent of an engineering challenge, especially because of the very large number of variables and interactions depend on the final results. The composition and structure of the soil in relation to the physico-chemical characteristics of the pollutant form specific systems that require certain approaches in the choice of depollution technologies [3], approaches that will be discussed in detail during the work.

2. SOIL POLLUTION WITH PETROLEUM PRODUCTS: SHORT CHARACTERIZATION OF THE PHENOMENON

The harmful effects of petroleum hydrocarbons on the environment and on the community may be among the most diverse; we can only mention the following:

- some compounds may affect taste and smell, so that their presence in surface water and groundwater, even in small quantities, makes them no longer suitable for consumption;
- volatile compounds can form explosive mixtures with oxygen in the air;
- some polyaromatic compounds have a carcinogenic effect and may be toxic;
- inhalation of vapors may lead to nausea, acute toxic reactions, liver problems.

In the Order of the Minister of Waters, Forests and Environmental Protection no. 756/1997 for the approval of the Regulation on the assessment of environmental pollution are presented as guidelines for the total oil content in soils the following: normal values: less than 100 mg/kg, alert values for susceptible polluted soils - 200 mg/kg, alert values for less sensitive soils - 1,000 mg/kg, intervention values for susceptible soils - 500 mg/kg and intervention values for less sensitive soils - 2,000 mg/kg.

Sensitive soils include all types of soils in residential and recreational areas, soils used for agricultural purposes and soils in underdeveloped areas. Less sensitive soils include all commercial and industrial types of soils and land areas that will be in use in the near future. Less polluting sources of pollution, including those generating oil pollution, are encountered at the level of less sensitive soils (see Fig. 1).

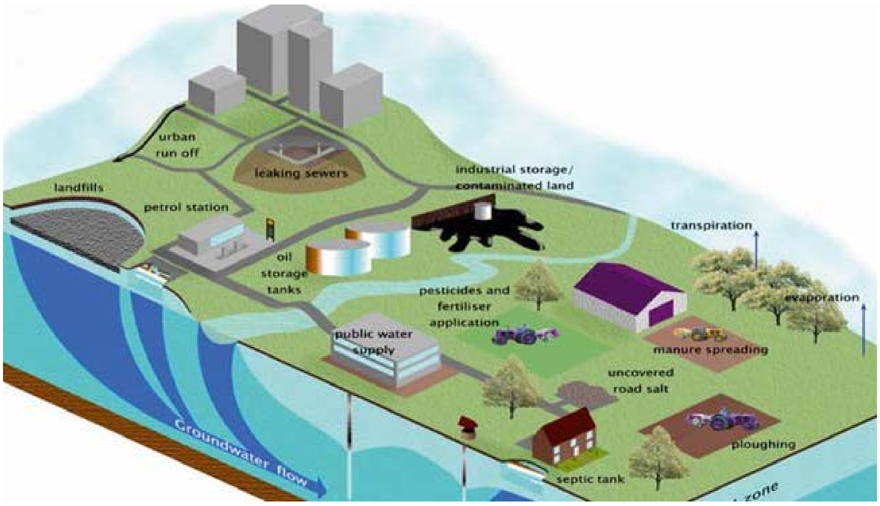

FIG. 1. The distribution of the main sources of pollution in soils with less sensitive use [2]

The toxicity of petroleum products is divided into two categories: immediate and long-term. Immediate is caused by saturated hydrocarbons which in high concentrations cause the death of organisms.

Aromatic hydrocarbons are the most toxic and olefinic hydrocarbons, in comparison with heavy metals [4], for example, have an intermediate toxicity between saturated and aromatic hydrocarbons. A method of classification which takes into account the nature of chemical pollutants is shown in Table 1.

Table 1. Classification of environmental pollutants (adapted by [4])

The nature of pollutants	Compartment / ecosystem affected			
	atmospheric	continental	limnos	marine
physical pollutants				
ionizing radiation	+	+	+	+
thermal pollution	+	+	+	+
chemical pollutants				
hydrocarbs	+	+	+	+
plastic materials		+	+	+
pesticides	+	+	+	+
detergents		+	+	+
…				
mineral particles	+	+		
heavy metals	+	+	+	+
other compounds of synthesis	+	+	+	+
biological pollutants				
dead organic matter	+	+	+	+

Long-term toxicity is due to the interference between hydrocarbons and soil components dissolved in water, interference with numerous chemical messengers, with the role of nutrition and reproduction of many aquatic organisms, for example, leading to ecological imbalances.

The profile distribution of the pollutant is dependent, in the vast majority of cases, on the quantity and characteristics of the pollutant, the configuration and characteristics of the soil and the residence time of the pollutant. In soils with poorly permeable or waterproof horizons, a pollutant concentration zone appears above (see Fig. 2), because by its polydisperse body properties, the soil acts as a chromatographic column.

FIG. 2. An example of an unwanted accident causing soil pollution with petroleum products

Petroleum components are retained especially in the higher horizons, and the film water accompanying the oil in varying proportions, with higher and less viscous density, penetrates faster in the lower horizons (see Fig. 3).

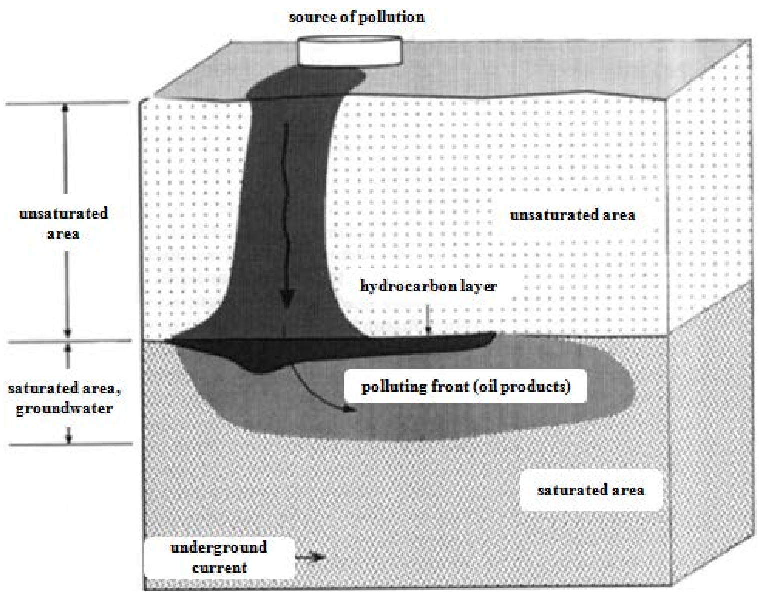

FIG. 3. Distribution and migration of a liquid petroleum product within a soil profile [8]

Petroleum volatile fractions containing 6-7 carbon atoms in the molecule are volatilized and non-volatile hydrocarbons tend to concentrate and solidify. As time passes, the process of redistribution of oil components on the soil profile is accentuated, with tars and asphaltenes being retained.

3. REMEDIATING OPPORTUNITIES FOR A SOIL CONTAMINATED WITH LIQUID PETROLEUM PRODUCTS

The phenomenon itself, the pollution of the environment with the fluids produced from the wells (crude oil, gas, condensation, salt water, sludges, sand), occurred with the start of the exploitation of crude oil and its use as an energy source.

Crude oil extraction and transport affect the environment both through the development of technological processes as well as by some undesirable accidents, such as tank discharges, overpasses or underground pipelines etc. The general technological flow specific to the crude oil - gas extraction and separation activity comprises the following important steps:

- the mixture of hydrocarbons in liquid and gaseous form with water and mechanical impurities is extracted through wells;
- the extracted fluids (crude oil, emulsified or free water, gas) are transported by pipeline to the separation / collection parks;
- separating the liquid phase (impurities - water from the deposit) from the gas phase is done in the separators of the scaffolding parks;
- the oil mixed with the sewage water, after gas separation, is provisionally stored in the park's tanks for disposal to the treatment and storage stations;
- rich gases are directed to the degazolination plant and the poor are directed to the internal consumption of the scaffolding or the gas distribution stations;
- the oil is treated thermo-chemically in the treatment tanks;
- wastewater is collected and reinjected through the injection wells.

The industrial objectives of oil exploration and separation are, according to [8, 10]: *oil and gas wells*, *separator parks*, *compressor stations*, *boiler batteries*, *storage facilities*, *wastewater collection plants*, *treatment plants*, *transport pipelines* and so on.

Pollution sources for environmental factors are the machines in which the basic activities of the scaffolding are carried out [2, 10]: *extraction*, *collection*, *separation*, *treatment*, *storage*, *transport* and machinery in which related activities are carried out: *production*, *steam distribution*, *wastewater treatment*, *water injection*, *sludge storage* etc.

Soil pollutants characterized by drilling, exploitation, separation, storage and transport of crude oil and gas can be: oil - which produces chemical pollution of the soil through radical changes (forming a waterproof film to prevent the exchange of gas), reservoir water - can cause changes in saturation, humus quality and microfauna degradation, detritus - has harmful action on crops due to the content of toxic metals: Cr, Ba and Cd, and drilling mud - has harmful action on crops due to heavy metals and salt contents.

Soil pollution with hydrocarbons from oil products directly hinders the processes of water infiltration into the soil, water circulation in the soil, and the exchange of gaseous substances with the atmosphere [5]. Indirectly, the activity of the entire edaphon being disrupted, vegetation on polluted soils develops with difficulty, and on the heavily polluted soils vegetation does not grow at all [5]. According to that, we must say that the type and composition of a particular petroleum fraction, through its specific properties, influences the mobility and retention of these fractions in the soil. Among the most important properties that can influence the soil-polluting behavior are density, dynamic viscosity, solubility and vapor pressure.

The density of petroleum products is lower than that of water, which may have an important effect on the flow and retention of oil products in wet and saturated soils; an increase in temperature tends to decrease density and viscosity and may increase the mobility of petroleum products in the soil.

Vapor pressure can be used to express the volatilization tendency of a liquid component; the degree of volatilization of a liquid gasoline depends on the vapor pressure of its components, the higher the vapor pressure, the volatility is stronger.

Adsorption refers to the binding of a component to the surface of an existing solid in the soil; when the components of the gasoline are present in a soil containing water, they will be distributed between the liquid phase and the dissolved phase, in proportion to the adsorption constants. In the layer near the soil surface, rich in organic matter, the adsorption increases directly in proportion to the organic matter content of the soil.

The main soil properties that influence the behavior of the soil-pollutant assembly and which we must take into account in the choice of depollution technologies are: *density and porosity*, *granulometry and capillary*, *moisture and suction*, *permeability and retention capacity*. Also, the state of the underground water, that can be affected, is characterized by *temporary hardness and pH*, *dissolved suspensions and gases*, *anion and metals content*, *radioactivity and corrosivity*, respectively by *electrical conductivity*, *microbiological content* and *organoleptic characteristics*.

We further consider as a case study an accidental pollution (breaking an overhead oil pipeline) into a chernozem. In these conditions, the determinants in the choice and application of a depollution technology are summarized in:

- the final degree of depollution, desired or imposed;
- duration of depollution actions;
- the total cost needed to carry out the depollution;
- the side effects produced during the application of depollution technologies and the effects arising after the application of the depollution process.

Knowing that the depollution technologies for soil contaminated with liquid petroleum products do not respond optimally, at the same time, to the four listed factors, we present and propose a number of possibilities for soil depollution according to our engineering knowledge so far.

Our proposals are summarized, as is natural, in the need to prioritize the choice of depollution technologies (starting with the minimal technology, continuing with the complex technology and ending with the one that we consider the best) depending on the concrete conditions in the field (we have to deal with a chernozem polluted with petroleum products) without considering a certain financial or technological capital.

For each of the 3 proposed (minimal, complex and optimal) depollution technologies to remedy the chernozem polluted with liquid petroleum products, we have decided to continue to expose a series of 3 sub-technologies (if we can call them in that way).

The minimal depollution technology with 3 possible variants includes, as simple as possible, minimal financial and, human and technological resources, removal of excess pollutants, excavation and sealing, and shows that:

- removal of excess pollutant is necessary as a first intervention in the case of accidental oil pollution and consists in removing hydrocarbons from the surface of the soil as quickly as possible to reduce the depth of penetration into the soil [1]. Collection pitches and small pits for concentration of the pollutant will be carried out in order to be collected by means of sorption systems in a tank and then transported to a treatment plant.
- excavation is applied in the case of accidental and point soil pollution [1] (as is the case with the pollution of a chernozem with liquid petroleum products), when the pollutant can shortly reach groundwater.
- sealing involves the physical closure of the contaminated environment by the use of a waterproofing system consisting of walls, quilt and bottom [1]; the objective is to stop the migration of pollutants by using physical barriers that counteract the effects of dispersion.

In addition to the technology of removing excess pollutants (see Fig. 4), it is necessary for the soil-removal technology, which is considered to be complex, as a result of financial and technological investments, the application of pumping depollution technology. This is used for the decontamination of soils contaminated with hydrocarbons floating at the interface between the saturated area and the unsaturated zone. It is also possible to call for hydraulic blocking, which involves stopping the migration of pollutants by installing water wells or wells, below the contaminated area and exhausting the water outdoors. If the depolar has consistent resources, we also consider the excavation to be auspicious.

FIG. 4. An example of technology involving the removal of excess pollutant (petroleum)

At the same time, we also welcome the application of absorbents, which has several main objectives, extremely well-defined, considering that we are talking about a polluted chernozem - sensitive soil (the alert value - 200 mg/kg) from our point of view:

- absorption of oil and its retention at the soil surface in order to be collected and sent to a recovery and treatment plant;
- retention of oil to prevent entry into the soil profile and thus hindering the remediation process;
- preventing the formation of waterproof film on the surface of the soil;
- stimulate multiplication of microorganisms involved in bioremediation.

An ultimate approach to be taken into consideration is also the enrichment of the oil-chernozem contaminated with selected microorganisms, which intensifies the triggering and development of biodegradation [6, 9]. Numerous biorem-technologies have been developed, including knowledge of biodegradation optimization pathways and the selection and use of microorganisms with superior degradation abilities [6, 7, 9].

The optimal environmental conditions required for the degradation of existing oil in a chernozem, according to numerous studies for the scientific literature, are: soil pH 6.5-8.0, humidity 30-90%, oxygen content 10-40% temperature 20-30°C and nutrient ratio C:N:P = 100:10:1. If the soil, whether it is a chernozem, is polluted with both oil and salt water, the bioremediation measures are combined with appropriate desalination measures, respectively, for washing the salts on the soil profile and capturing the water washing in a drainage system to be treated before discharge into the emissary.

4. ECO-TECHNOLOGY RECOMMENDATIONS

Taking into account the previously mentioned statements regarding the ways of polluting soils with liquid petroleum products, we should synthetically present a series of eco-technological recommendations, unconditionally applied on polluted soil, as follows:

- ✓ digging ditches for the rapid collection of petroleum hydrocarbon spread on land and transporting it to a treatment and recovery facility;
- ✓ application of 16 t/ha of peat to absorb the remaining oil and to limit its penetration into the soil, to soil the soil and to stimulate the development of hydrocarbon degrading microorganisms;
- ✓ loosen the soil by repeatedly tapping with the cutter and the disc at a depth of 25 cm to ensure aeration;
- ✓ if the soil is acidic or basic it is recommended to apply the amendments and incorporate them into the soil;
- ✓ fertilization with 150 t/ha of fermented or compost manure by applying it as homogeneous to the polluted land;
- ✓ fertilize with mineral fertilizers, especially humate-based liquids at 650 l/ha, which differ according to soil characteristics;
- ✓ the field is recommended to be cultivated with corn, lucerne, barley, oats and other mixtures of grasses, which are suitable for the specifics of the area.

CONCLUSIONS

Pollution of soils and aquifers with petroleum products is a category of frequently encountered incidents with significant environmental and economic consequences. In most cases of soil pollution, the negative effects extend shortly from production to both the subsoil, groundwater, infiltration and the atmosphere by evaporation of highly volatile pollutant compounds.

The problem of depolluting soils contaminated with oil products is one of the most complex activities in the field of environmental protection, both theoretically, economically and organizationally. The large number of factors that influence the processes and the inappropriate way in which they are addressed, leading to situations where the results expected from the depollution are not obtained.

If we are talking about optimal depollution technologies, optimizing the activity in this area involves compromising the results obtained by applying a depollution technology and the financial, material and human efforts that have made these results. The decision-maker or the depollution technology manager, is the person or organizational structure over which the ultimate responsibility is most often focused. The comparative analysis of the advantages and disadvantages of each category of depollution technologies should be done in relation to a list of priority objectives set according to the specific pollution conditions. The results of such analysis must guide the final solution to variant that corresponds in a given context.

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