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The contamination of the soil with petroleum products and identification of environmental risks

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Abstract. The petroleum products are a group of substances widely spread all around the world. The petroleum exploitation, in most of the cases leads to the contamination of the sites by natural sources and anthropogenic ones. At a national level, the pollution with petroleum products and salted water outcome from the petroleum exploitations and transport is spread on approximately 50 thousand ha. Due to the pollutants' migration to the non-saturated area, certain fractions of the formed body of impregnation can be mobilized towards the atmosphere or towards the aquifer causing negative effects upon the populations' health and the environment. The evaluation of the risks due to petroleum products, by means of conceptual systems according to the existent norms, implies a complex qualitative and quantitative analyze of the available data of the contaminated site, in order to see the risks caused by these. The risks' analysis is necessary for establishing the optimum technology in order to depollute the contaminated sites.

Key Words: the evaluation of risks, petroleum products, contaminated sites, the pollutants' migration.

Introduction. The petroleum extractive industry has a complex activity including a wide paddle of pollution sources. The pollution of sites can take place both through natural sources (e.g. petroleum wells) and anthropogenic ones (e.g. the extraction and processing industry, the residual waters from the petroleum refinery, the imperviousness defects in the pipes, the lickings from the corroded tanks, the surpassing of the tanks' capacity of storage during the filling, the system of transportation etc.) (Dumitran & Nicolescu 2008).

In order to have a more detailed vision at a national level, on the contaminated sites, it will be presented their distribution, on areas of activity through the Figure 1 (Băceanu 2011).

After analyzing the eight existing areas in Romania (North-East – Bacău; South-East – Galaţi; South Muntenia – Piteşti; South-West Oltenia – Craiova; West Timişoara; North-West – Cluj-Napoca; Center - Sibiu; Bucharest – Ilfov) the graphic of the sites contaminated with petroleum products will be made (Figure 2).

With the passage of time, history has proven that petroleum can be both a factor of progress and regress, and by definition it can be a mixture of hydrocarbons, volatiles and semi-volatiles (Tudorache 2010).

The main categories of petroleum hydrocarbons are those such as: the raw petrol, the natural gas, the pitch and the bitumen (asphalt) which they also contain different quantities of alkanes (e.g. methane, ethane, propane), aromatic hydrocarbons (benzene, toluene, ethylbenzene and xylene, group also known by the name of BTEX) and polycyclic aromatic hydrocarbons (PAH, e.g. naphthalene, phenanthrene, anthracene).

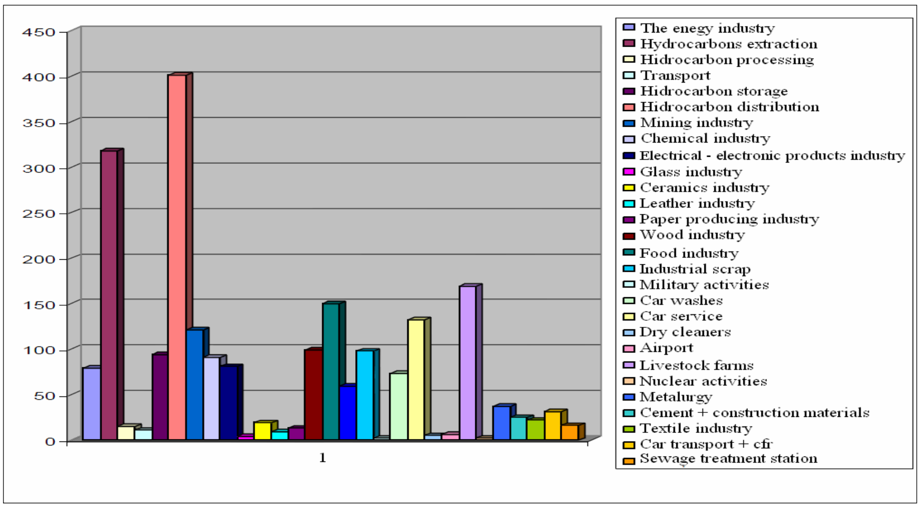

Figure 1. The distribution of sites on areas of contamination.

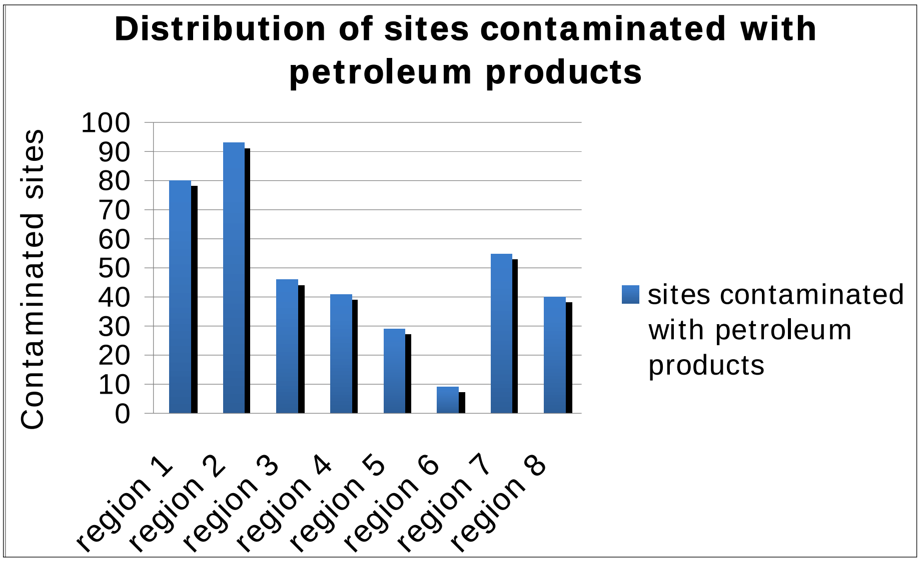

Figure 2. The distribution on regions of the sites contaminated with petroleum products.

The main values of reference for the hydrocarbons originating form petroleum are given in Table 1.

Table 1

Hydrocarbons values from petroleum (mg kg^{-1} dry substance) (Decree no. 756/1997)

Trails of elements	Normal values	Allert treshold/ Types of usages		Intervention treshold/ Types of usages	
		Sensitive	Less sensitive	Sensitive	Less sensitive
Overall of hydrocarbons from petroleum	< 100	200	1000	500	2000

The migration of the petroleum products into the subterranean environment. The subterranean environment has in its composition minerals and rocks of different granulometric dimensions, provided with pores which through interconnection allow the water to circulate. In the composition of the underground environment there are included two areas: a saturated and a non-saturated area (aquifer) (Micle 2009).

Due to pollution with petroleum products the pollutant, in the non-saturated area, forms a body of impregnation from which certain fractions can be mobilized towards the atmosphere or the aquifer (Figure 3).

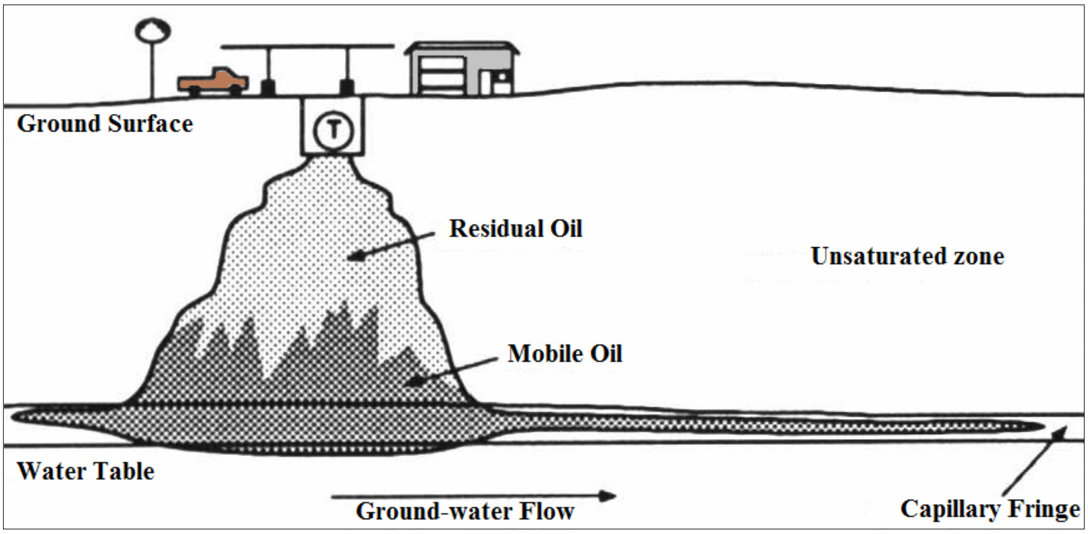

Figure 3. The migration LANPL (combustible, light oils) poured into subterranean environment, which leads to the sudden loss of a high quantity of petroleum from the tank of subterranean storage (Beck 1996).

At contact with the saturated area, step by step the polluting forms a thin floating web situated at the interface between the two areas.

The surface of the floating web of pollutant can be calculated with the following formulae and its form depends on the running speed of the subterranean water and the properties of the rocks found at the interface of the two areas (Micle & Neag 2009):

$$S = \frac{1000 \times (V_i - V_r)}{g_p} \text{ [m}^2\text{] (1)}$$

where: V_i – the total volume of the infiltrated polluting, m^3;
V_r – the volume of polluting retained by the non-saturated area, m^3;
g_p – the maximum thickness of the floating web of polluting, mm.

The negative effects of the pollution with petroleum products. The physical, chemical and biological phenomena influence the transport of pollutants in the soil, in the surface waters, aquifer, air, modifying their normal characteristics (Neag 1997).

The negative effects of pollution (Figure 4) may have influences upon: the soil/subterranean from inside the park of the separators, of the pits; the soil and subterranean near the well, the park and the station of injection; the course of surface waters and the subterranean water (aquifer) (Dumitran & Nicolescu 2008).

The flowed petroleum contains hydrocarbons, which are polluting substances that affect on a long-term and can destroy the composition of the trophic chains. A better knowledge of the impact and discharge of petroleum can have a major impact in the management and fight against the effects upon the environment and the population's life (Brebeanu 2005).

Figure 4. The pollution with petroleum products: a) and b) Aninoasa place, pollution due to the scrapping of an ancient well of petroleum exploitation (www.oglindagorjului.ro/?p=761; www.ecomagazin.ro); c) Pietriş Village, Poiana Câmpina, pollution resulted from more than 60 petroleum extraction wells (www.presaonline.com).

The evaluation of the risks of the environment pollution. The evaluation of the risks upon the environment (ERA) implies the critical analysis of the available data in order to determine the possible risks associated with a potential threat (Dumitran & Onuţu 2010).

In the case of industrial sites, the evaluation of risks from a qualitative and quantitative point of view is complex and it requires more data. The quantitative evaluation is a technique difficult to make because it involves substantial costs (Neag 1997).

The general purpose of the evaluation of risks is to control the risks resulting from a location, by identifying: the polluting factors or the biggest dangers; the resources and the receivers exposed to risks; the mechanisms through which the risk is produced; the important risks which occur on a location; the general preventions in order to diminish the grade of risk at an acceptable level.

The risk of the contaminators (PAH) is evaluated based upon their toxicity and their exposure. Due to the lightness of the molecular weight of PAH, it is considered directly toxic, and the compounds HMW PAH are considered genotoxic, or capable of provoking damages to the DNA. Toxicity is mainly the result of the metabolic transformations of PAH in the human body in a complex mixture of quinones, quinines, cis- and trans-dihydrodiols, phenols, epoxides and other oxidized metabolites according to the hydrocarbons and the metabolic layout (Volkering & Breure 2003; Wick et al 2011)

The main doses of reference and analytical methods of hydrocarbons fractions are presented in Table 2 (Daniels & Easterly 2010).

Table 2

Reference doses and analytical methods of hydrocarbons

Hydrocarbon fractions	*Substitute*	*Reference dose ($mg\ kg^{-1}\ day^{-1}$)*		*Analytical method***
Aliphatic		*Oral*	*Inhalation*	
EC* 5-6	Cyclohexane	1.7	1.7	VPH
EC > 6-8	Cyclohexane	1.7	1.7	VPH
EC > 8-10	JP – 8	0.03	0.085	VPH/EPH
EC > 10-12	JP – 8	0.03	0.085	VPH/EPH
EC > 12-16	JP – 8	0.03	0.085	EPH
EC > 16-21	White mineral oil	2.0	NA	EPH
EC > 21-34	White mineral oil	2.0	NA	EPH
Aromatic				
EC 8-10	Izopropyl-benzene	0.1	0.1	VPH
EC > 10-12	1,1 biphenyl	0.05	0.06	VPH/EPH
EC > 12-16	1,1 biphenyl	0.05	0.06	EPH
EC > 16-21	Pyrene	0.03	NA	EPH
EC > 21-34	Pyrene	0.03	NA	EPH

*EC – carbon equivalent; **VPH – volatile petroleum hydrocarbons; EPH – extractable petroleum hydrocarbons.

People can, in both cases, be exposed through ingestion, inhalation and dermal exposure by: the consume of contaminated water; the consume of plants and animals which came in contact with contaminators; the inspiration of PAH particles; holding in hand the soil contaminated with PAH.

The PAH compounds at contact with people are distributed, metabolized and stocked in the human body. Once the compounds reach the human body they can cause: effects on the respiratory system, the reproductive system, neurological system, malformed and cancer (Figure 5) (Wick et al 2011).

EPA has elaborated the criteria of the risks base (RBC) and the level of screening (SSLs) of the soil in order to determinate and the minimization of the risks associated to certain contaminators.

The level of screening of the soil is an expression of the red blood corpuscles and it was initially developed as an instrument for the generic standardization and acceleration of the contaminated sites remediation for the future utilization of the residential lands.

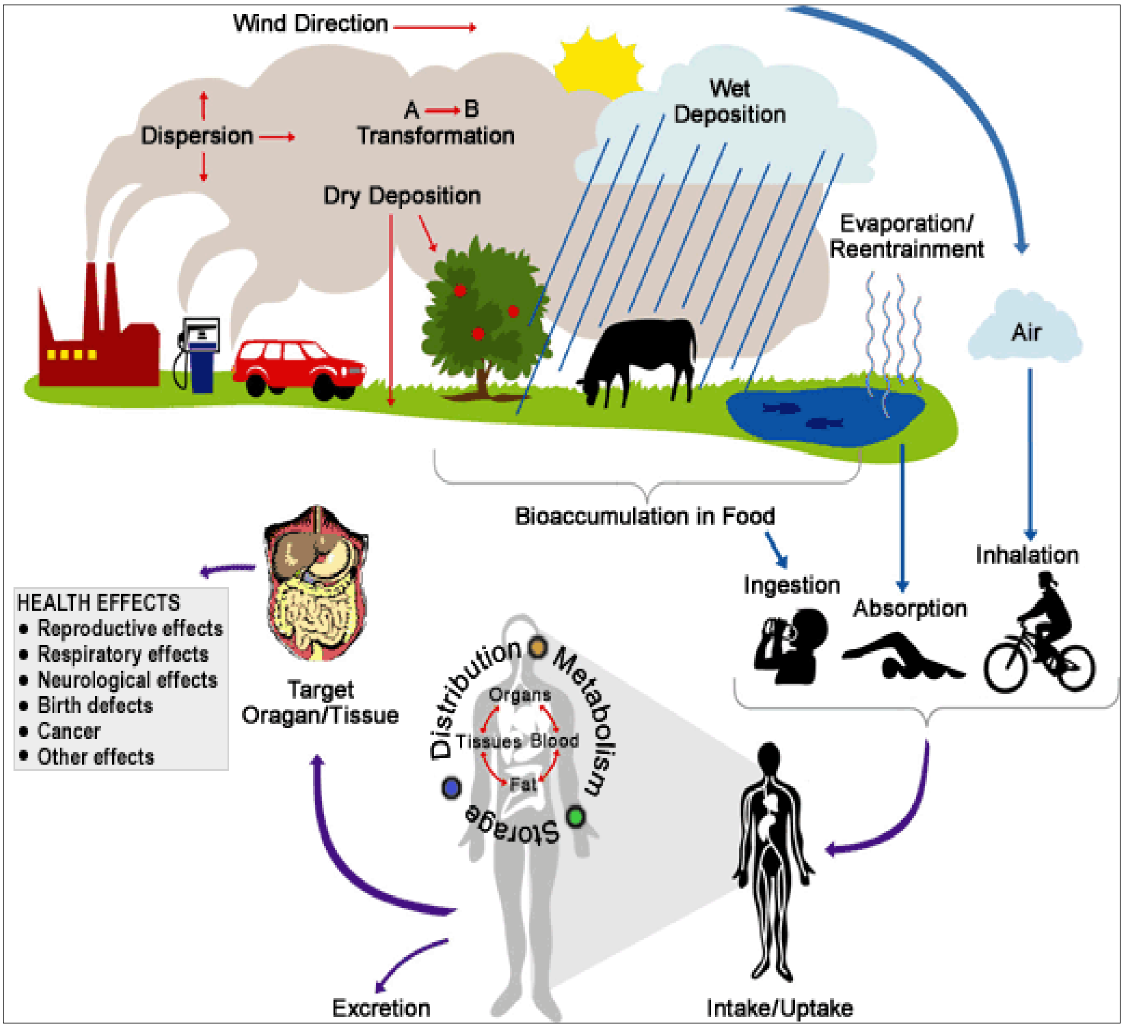

Figure 5. The basis risks of exposure to contaminators (source: www.in.gov/idem/risk/).

The equation of the basic criteria of risk (RBCs) combines the ways of human exposure with the toxicity data related by EPA for the determination of SSLs for contaminated sites. To these equations different values can be implemented in order to make the RBCs specific for every contaminated site (EPA 1996). In the evaluation of an ingested cancerous genetic material from a residential soil, the following equation is used (EPA 2003):

$$RBC = \frac{TR \cdot AT_C}{EF_r \cdot \left(IFS_{adj} / 10^6 \cdot CSF_o\right)} \quad (2)$$

in which:

RBC – the basic criteria of risks [mg kg^{-1}];

TR – the target of the cancer risk (standard value=1*10^{-6});

AT_c – the medium time of exposure to cancerous factors (365 days/year*70 years = 25550);

EF_r – the frequence of exposure [days $year^{-1}$];

IFS_{adj} – the age ajusted to the soil of the indigestion factor [mg year kg^{-1} day^{-1} (114.29)];

CSF_o – the pitch of the oral cancer risk factor [mg kg^{-1} day^{-1}].

Compared with the way of manipulation, the conceptual systems can be, also, developed with specific information concerning the site which is meant to be remediated, with the help of the following parameters of the soil: density, the quantity of clay or organic substances. Due to the fact that the connections between pollutants and the organic substances, clay and the porosity of the soil (expressed as density), influence the distruction of the aromatic polyciclic hydrocarbons (PAH), the properties of these soils have a major importance for establishing the remediation methods (Wick et al 2011).

Conclusions. At a national level, by analyzing the specialised literature, concerning the eight regions, we have proven the vast contamination of sites with petroleum products.

With the passage of time, history has shown that the activity of petroleum extraction damages the environmet, causing harmful effects both upon the soil and the subterranean, as upon the humans and the animals by the plants' absorbtion of contaminants.

As a result of the evaluation of risks, the undesired risks can be identified both on humans (e.g. respiratory impact, on reproduction, on the neurological system, birth disabilities and cancer) and on the envrionment (e.g. the destruction on long term of the trophique chains' composition).

The bibliographic analysis of the risks of pollution was made with the purpose of demonstrationg the connection between pollutants and organic substances, clay, the soils' porosity and the influence of the parameters, in order to reduce the risks by means of finding an optimum technology of decontamination.

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