ORIGINAL RESEARCH PAPER

HYDROCARBONS DIAGNOSTIC OF POLLUTED SOILS

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Abstract: Petroleum hydrocarbons are known as carcinogenic and may contaminate the environment (water, air and soil). In this study, a diagnostic of polluted soils by petroleum hydrocarbons is carried out in order to know the effect of their accumulation as well as their behavior in time. The aging factor, a source of significant changing in hydrocarbon behavior, is integrated on two sites of an industrial refinery as experimental samples. The first site is recently polluted by hydrocarbons while the second is a previously polluted site.

The results indicate that the concentration of hydrocarbons on the surface of the first site is greater and remains stable in time, as for the second site, hydrocarbons concentration on the surface is also important and undergoes a weak reduction. At a depth of one meter hydrocarbons exist at a greater concentration. This shows that obstinate hydrocarbons are an environmental danger for fauna and flora.

Keywords: *petroleum hydrocarbons, pyrolytic, carcinogenic, diagnostic, accumulation, behaviors*

INTRODUCTION

In industrial countries, pollution by oil products is a major environmental, economic and human problem: crude oil is made up of different compound families of whose chemical composition varies according to their geographical and geological origin, Tissot and Welte [1] quote the average composition of 527 crude oil samples as 58.2% saturated, 28.6% aromatic and 14.2% polar compounds. Hydrocarbons represent 65 to 95% of crude oil and constitute a large chemical domain, such as gasoline, kerosene, fuel, gas, jet … etc. Generally, carbonaceous species are a very important fraction of ambient aerosols ranging from 20 – 80% [2 – 3]. This organic fraction is made up of a mixture of compounds including aliphatic, aromatics, aldehydes, ketones, acids and nitrates, whose nature is still scarcely known [4]. In addition to this organic species, the production and use of different petroleum derivatives generates a widespread contamination of soil and facilitates their handling [5]. The growing scientific interest in the study of this organic aerosol fraction results from the fact that it may contain toxic organic species and therefore have diverse effect on human health.

In addition, the use of these products is likely to contaminate all environment levels (air, water and soil), but the crossing of this contaminant to the soil remains an important stage and can be influenced by different phenomena. The intrinsic degradation and the scattering of hydrocarbons are competitive phenomena that can be noticed once they reach the soil. The volatilization, the phenomenon of scattering in the air and the streaming infiltration generate the pollution of surface water and groundwater respectively; all these cause a loss of physical-chemical characteristics of soil, as well as the pollution of the water table. Therefore it is crucial to study hydrocarbons on different soils, in order to understand and to predict their later distribution or future transformation.

Many investigations have focused on cleaning up contaminated sites, by treating the soil or allowing natural degradation process to degrade the residual contaminant, provided that the soil can be considered as "biostabilized" [6]. However, this phenomenon requires an understanding of processes that limit degradation. Many factors influence the feasibility and effectiveness of bioremediation in the presence of microorganisms, the availability of nutrient, temperature and pH. It's well known that low temperatures reduce microbial activity. There is generally a positive correlation between temperature and biodegradation [7 – 8]. Besides, [9] indicated that more crude oil could be removed if temperature was increased beyond 50 °C. The increase of temperature reduces oil viscosity, consequently increasing oil mobility. Compositional analysis of microbial biomass shows that carbon, nitrogen, and phosphorous are present in the ratio of ca. 106:16:1 respectively [10]. Different nutrient levels or amendments result in a range of degradation rate due to the tight relationship between nutrient and water concentrations in the soil matrix [11]. Also was noted that the soil type was an important factor influencing water holding capacity and nutrient concentration in the soil water. The weight of these factors on these pollutants behavior is to be investigated.

In this work, the distribution of hydrocarbons that contaminate the soils and their change in time was monitored. The purpose is to gain information on hydrocarbon concentration in the site of interest in order to evaluate the likely correlation between soil physical-chemical properties, the hydrocarbon level, and the meteorological

conditions, the impact of these factors on the elimination of these pollutants is to be examined. This work is based on a SAMI's refinery soil that was contaminated by petroleum hydrocarbons. The aging factor that can change significantly the hydrocarbons behavior and evolution of these soil pollutants in time is integrated (Figure 1).
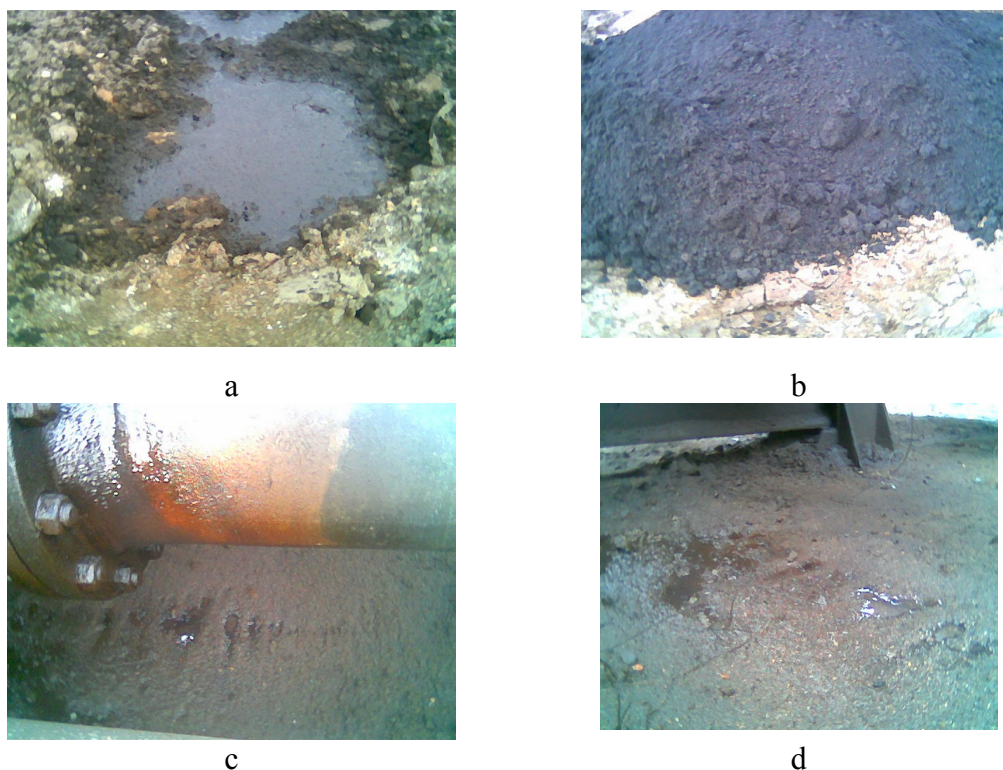

Figure 1. *Polluted soils in the first (a, b) and second site (c, d)*

EXPERIMENT DESIGN

Area description

The contaminated soil is obtained by composite samples from industrial sites (the industrial refinery) near the Atlantic Ocean. The climate is Mediterranean continental, characterized by low temperatures during winter and high temperatures during summer. The selected pilot soils usually correspond to current field situation, and integrate the pollutant aging factor, source of significant changing hydrocarbon behavior. An inquiry on land was led, using a questionnaire to support this work, which concerns: the different polluted zones, the hydrocarbon types polluting the soil, and the origin and the age of the pollutants. The results of this investigation show that we have two sites polluted with hydrocarbons that have a petroleum origin. The first site (dump) was formerly polluted by hydrocarbons caused by a petrol leak and fire that occurred in 2002, see Figure 1 (a, b). The second site was recently polluted by different sources of hydrocarbons leaking from pipes that contained kerosene, gasoline, gas, jet and diesel; see Figure 1 (c, d).

Sample collection

This research was conducted in the summer season. The soil samples were collected from the first site on the surface and at a depth of one meter according to the soils color, and these pollutants were accumulated in time. The other soil samples receiving direct impact were collected from the surface of the second site. All the soil samples were retained in sterilized plastic bags and stored in a refrigerator at 4 °C in our laboratory before being analyzed.

Analytical procedures

Sample soils were defrosted, air-dried and passed through a sieve (2 mm) to remove gravel and rubbish according to AFNOR norm [12]. The pH was measured with pH Crison meter (Micro PH 2000) by the determination of the pH of a soil suspension in water (ratio weight/volume = 2/5), according to the norm French Industrial Standards Authority X 31 – 103 [13]. The conductivity was determined with a Crison conductivity meter model 522 in a soil/water slurry (w/v = 1/10). Soil water relates was determined after drying at 105 °C of defined weight wet soil. The organic carbon was measured according to the norm French Industrial Standards Authority X 31 – 109 [14]. The sample soils passed through a sifter of 315. The required tests for the determination of the organic carbon varied according to the presumed content of the carbon. The dosage principle was the carbon oxidization of the organic matter by the potassium dichromate in excess, in acidic medium at 135 °C; the remaining dichromate excess was measured by titration with a solution of Mohr salt. This rate in organic carbon allows estimating the rate in organic matter multiplying the result by 2 [15]. However, these coefficient multipliers are not perfectly adapted to all organic matters; notably forest. The soil nitrogen content was determined by Kjeldahl procedure. This method consists of a heating mineralization by sulfuric acid, followed by a distillation in a basic medium and titration with sulfuric acid. The soil phosphorus content was determined by a heat mineralization in *aqua regis* (HCl – HNO$_3$) and the concentration was determined by UV spectroscopy. Tables 1 and 2 present the physical-chemical characterization of the soils respectively of the first and second sites.
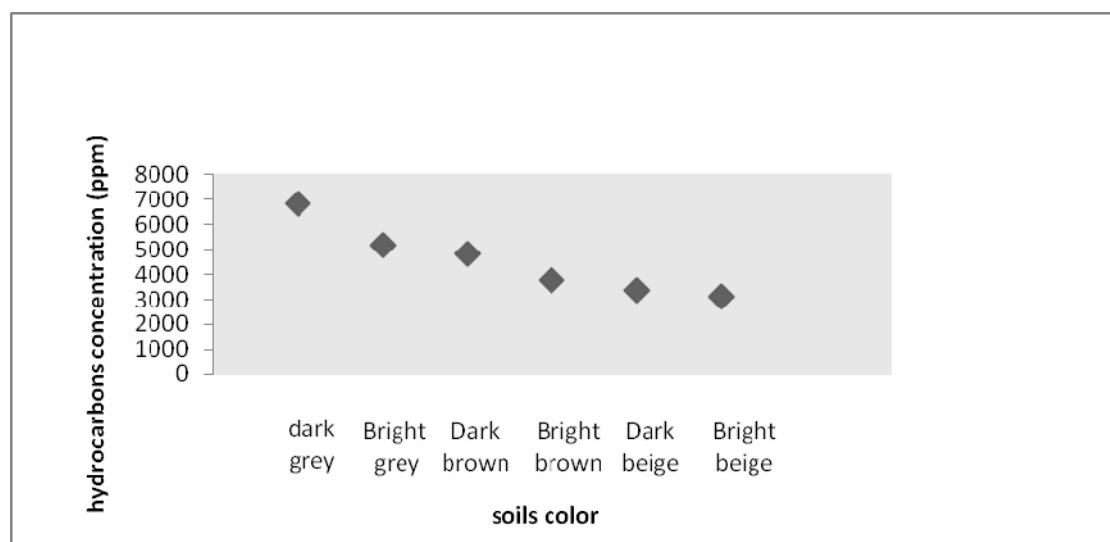
Table 1. *Soil chemical properties at the first site*

Characteristics	Soil sample					
	Grey	Dark Brown	Bright Beige	Bright Brown	Dark Beige	Dark Grey
pH	6	6.7	7.25	7.3	7.65	7.8
Conductivity [mS.cm^{-1}]	1750	1560	1030	2020	1800	1750
Organic carbon [%]	29.16	27.36	23.14	27.26	25.80	39.3
Water content [%]	10.2	16.8	13	12.6	18.5	22
Kjeldahl nitrogen [%]	2.3	3.05	1.96	2.01	0.84	1.12
Total phosphorus [%]	0.5	0.8	0.9	0.4	1.0	1.2

Table 2. Soil chemical properties at the second site

Sampler	Characteristics					
	*p*H	Conductivity [mS.cm^{-1}]	Organic carbon [%]	Water content [%]	Kjeldahl nitrogen [%]	Total phosphorus [%]
Gas	7.61	1488	14.1	9	1.6	0.2
Kerosene	7.63	1560	21.8	14	2.3	0.4
Fuel	7.59	1039	23.4	9	0.98	0.8
Diesel	7.63	1652	26.8	13	1.64	0.9
Gasoline	7.65	1230	23.6	13	1.78	0.8
Crude oil	7.60	2015	27.3	11	1.23	1.0

Analysis of hydrocarbons

The determination of hydrocarbons soil was carried at the day of sampling. For extraction, 25 g of wet soils was mixed with 50 mL of carbon tetrachloride (CCl_4) during 15 min; the mixture was let to decant for 30 min. The liquid phase obtained was filtered through a paper filter Whatman GF/A glass micro fiber containing sodium sulphate (Na_2SO_4) in order to retain all traces of water. The filtered extract was passed through a silica column in order to retain all organic matter without hydrocarbons. Finally, hydrocarbons concentration was measured by Infrared Spectrophotometer (Figures 2 and 3).

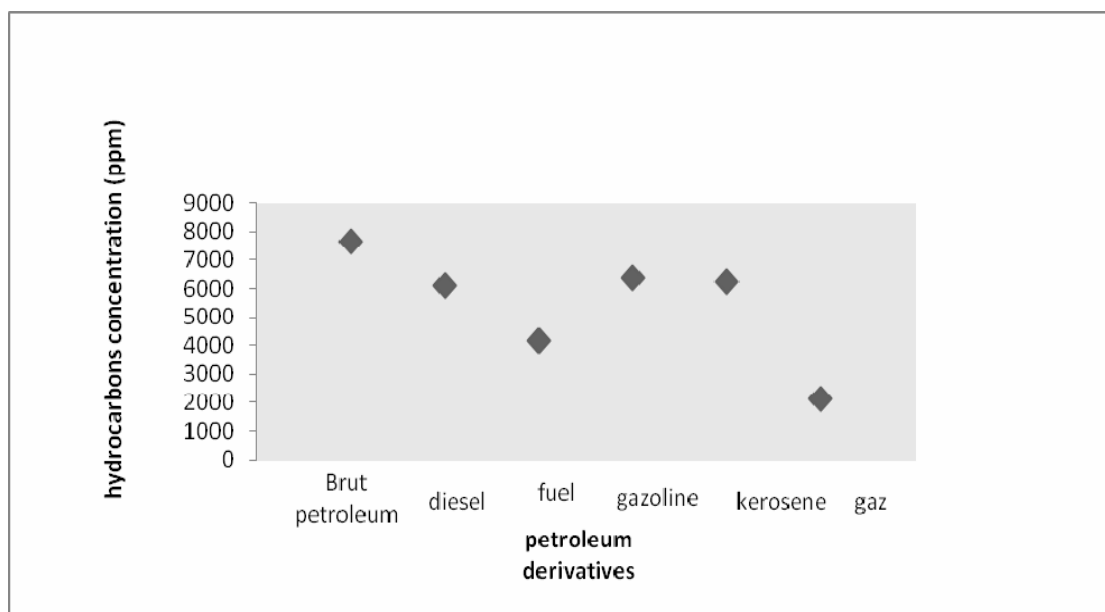***Figure 2.*** *Hydrocarbons concentration in the surface of the first site*

Figure 3. Hydrocarbons concentration in the surface of the second site

RESULTS AND DISCUSSION

Physical characteristics of soil

The granulometric analysis shows that sands are the major fraction of both soils, with more than 76% of the soil, and more than 15% is loam in the both cases. The experimented soils show that they are very sandy soils according to the textural triangle of grouping studies of the Pedology Problems [16] textural triangle [15]; the classification used in the international literature gives the same denominations for the two cases as sandy loam.

Chemical characteristics of soil

Tables 1 and 2 are presenting the chemical analyses respectively of the first and second soils. These analyses indicate that phosphorous in soil is not adequate in comparison to the optimal target 106:10:1. The found values of the C/N, show that these soils are of agricultural type [18]; in the both sites the soil pH was neutral. The pH in the first site is between 6.9 and 7.6 and in the second site between 7.5 and 7.6, the pH of the soils being in limit inferior to the pH basic fixed by the referential pedological [19].

Hydrocarbon distribution

Despite the identical geological characteristic and meteorological condition in the two sites, the comparison of hydrocarbon concentration differs according to the composition of the pollutants. The general idea of this study shows the distribution of these pollutants and their behavior in time, Figures 2 and 3 exhibit hydrocarbons concentration respectively to the surface of the first and second site. The hydrocarbons

concentration is found to vary dramatically. The results indicate that hydrocarbons that exist in our sites have a relatively greater abundance and the level of pollutants differs according to their dispersion. Generally, hydrocarbon concentration on the surface of both sites is the same. This test shows no significant difference between the average concentration values; in the first site, the dark color samples are more contaminated in comparison to those of bright coloration, and are compatible to our result. The sample that has a dark grey color is polluted more than the one that has a bright grey color, in the same way for the other samples of other colors (Brown and Beige). The grey color samples contain more hydrocarbons than the brown ones, so the beige color samples contain the least of hydrocarbons. In the second site, statistics also show that there is a difference in the hydrocarbons distribution. The sample polluted by petroleum contains greater hydrocarbons concentration, and the other samples have also important amounts of hydrocarbons, so the sample polluted by gasoline is respectively more contaminated than those contaminated either by kerosene, diesel or gas. This phenomenon can be determined by the degree of leak as well as the chemical composition of contaminant.
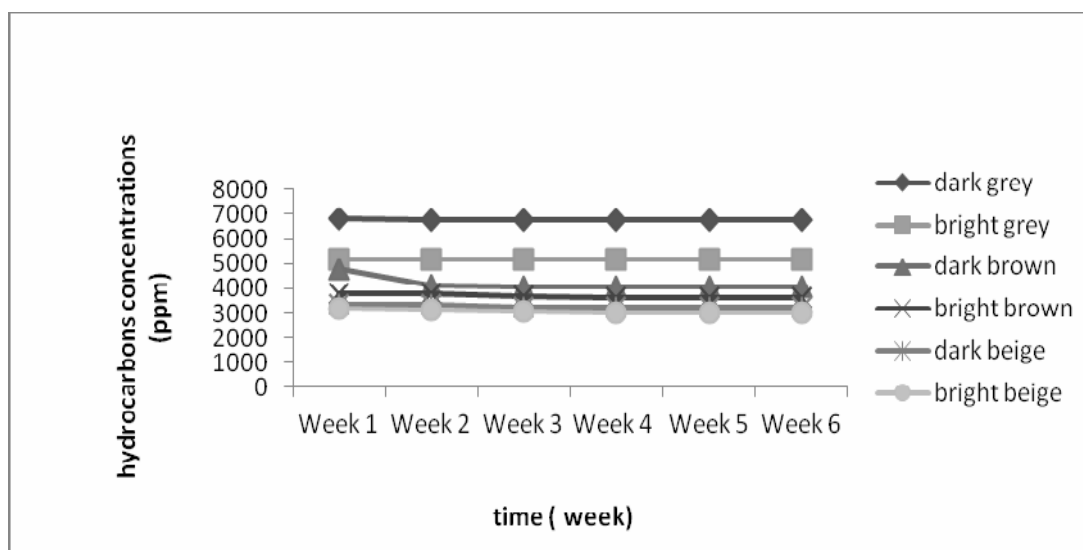

Figure 4. Evolution of hydrocarbons concentration in the first site
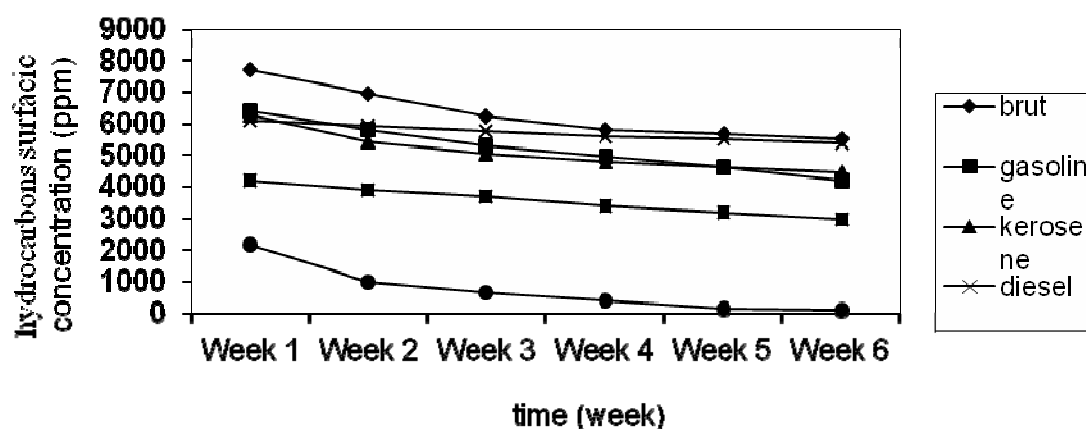

Figure 5. Evolution of hydrocarbons concentration in the second site

The results of our experiment reveal that hydrocarbons can be easily eliminated from soil while others can persist in the natural phenomena, as well as their presence at great amount in the soil. Figures 4 and 5 are showing the follow up of hydrocarbons concentration during six weeks on the surface of the first and second site. The observation of the first site reveals that hydrocarbons concentration doesn't undergo a big reduction. This concentration is nearly steady; it looks logical because this site was polluted formerly; these contaminants can already be influenced by different similar natural phenomena, such as evaporation, photodegrading, intrinsic biodegrading, infiltration toward the underground … etc, whereas in the recently polluted second site, a reduction of hydrocarbons concentration is undergone at different levels. It seems logical since the petroleum derivatives have various compositions so their hydrocarbons decrease differently. Hydrocarbons from diesel don't undergo a big reduction in comparison with the other from petroleum derivatives, such as kerosene and gasoline. On the other hand, the hydrocarbons proceeded by gas/petrol undergo a big reduction of their concentration because the gas/petrol contains hydrocarbons of weak molecular weight, that are easily degradable and can therefore vanish.
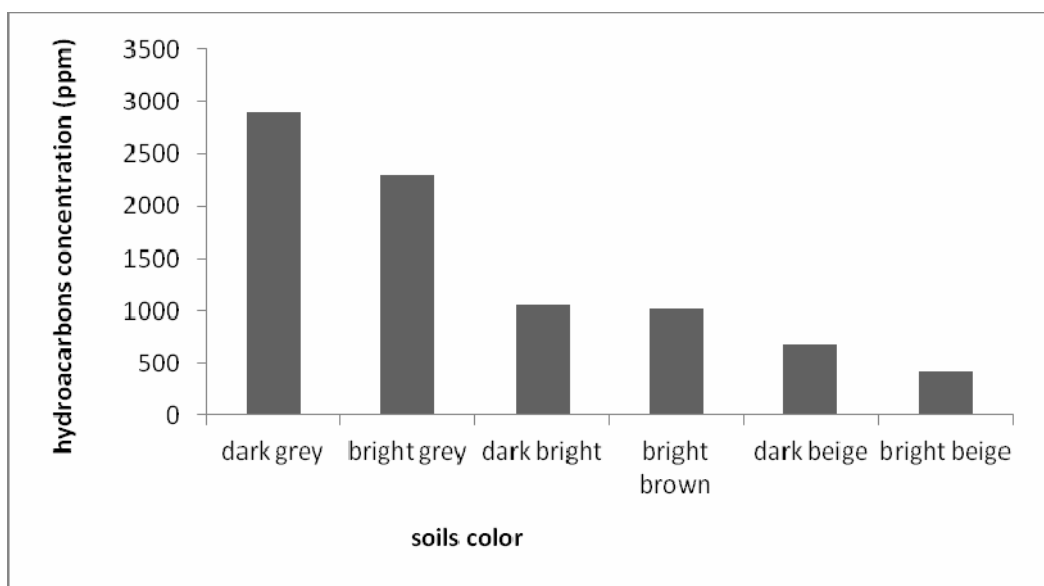

Figure 6. *Hydrocarbons concentration at a depth of one meter in the first site*

In the first site, Figure 6 reveals hydrocarbons concentration at a depth of one meter for at different points. We noticed an important amount of hydrocarbons at different concentrations, so that the soil physical-chemical properties are unfavorable to the hydrocarbons biodegradation. The lack of phosphor prevents the microbial activity and the sand considerably diminishes the effects of media characteristics. Physical phenomenon such as absorption might have limited microbial removal rate. The types of soil and the accumulation of these contaminants in time can generate an infiltration of hydrocarbons at the surface toward the under soil, and these contaminants can reach the water table. In addition to the climatic conditions, the interactions between wind and temperature cause drying and strong scattering of the constituent of the soil surface, so there is hydrocarbons immigration toward other places. All these require a cleaning for

the elimination of these pollutants in order to not have any secondary effects on the environment.

CONCLUSIONS

This research is to study the abundance of the petroleum hydrocarbons pollutant of two sites of an industrial refinery, as well as the behavior of these contaminants in time. In the first stage, the interest is focused on physical-chemical properties of polluted soil with hydrocarbons and the degree of these contaminations at different points of the sites. In the second stage, the evolution of hydrocarbons concentration is followed for six weeks.

The result of this experiment shows a large abundance of these hydrocarbons in the both sites and some of them can disappear in time, while others persist and don't undergo a big reduction. So the initial amount of hydrocarbons in soils influences significantly the level of the pollutant degradation. The polycyclic aromatic hydrocarbons (PAH) of large molecular weight are strongly absorbed to the organic matter, therefore less available to microbial metabolism [20]. Furthermore, the volatilization cannot reach all types of hydrocarbons; especially those of large molecular weight [21] demonstrate clearly the insignificance of volatilization as a contributing factor in the total petroleum hydrocarbons (TPH) removal during their study. As a conclusion, taking into consideration the approval of the authors and the result of this research, one can say that if these contaminants are let to their fate; they can present a great danger on fauna and flora. Therefore these sites require a rigorous treatment in order to avoid all negative effects on the environment.

ACKNOWLEDGMENTS

REFERENCES

1. Tissot, B.P., Welte, D.H.: *Petroleum Formation and Occurence*, Springer-Verlag, Berlin, **1984**;
2. Chow, J.U.C., Watson, Fujita, E.M., Lu, Z.Q., Lawson, D.R., Ashbaugh, L.L.: Temporal and spatial distributions of PM2.5 and PM10 aerosol in the southern California Air Quality Study, *Atmospheric Environment*, **1994**, **28**, 2061-2080;
3. Zheng, M., Wan, T.S.M., Fang, M., Wang, F.: Characterization of the non-volatile organic compounds in the aerosols of Hong Kong – identification, abundance and origin, *Atmospheric Environment*, **1997**, **31**, 227-237;
4. Alves, C., Pio, C., Duarte, A.: Particle size distributed organic compounds in a forest atmosphere, *Environmental Science and Technology*, **2000**, **27**, 4287-4293;
5. Barbee, G.D., Brown, K.W., Donelly, K.C.: Fate of mutagenic chemicals in soil amended with petroleum and wood preserving sludges, *Waste Management and Research*, **1992**, **10**, 73-85;
6. Luthy, R.G., Aiken, G.R., Sims, J.L., Reinhard, M., Traina, S.J., Weber Jr., Westall, J.C: Sequestration of hydrophobic organic contaminants by geosorbents, *Environ. Sci. Technol.*, **1997**, **31**, 3341-3347;

7.   Atlas, R.M.: Microbial degradation of petroleum hydrocarbons: an environmental perspective, *Micribiol. Rev.*, **1981**, <u>45</u> (1), 180 – 209;
8.   Morita, R.Y.: Low temperature environments in: *Encyclopaedia of Microbiology*, (Lederberg, J. ed.), Academic Press, New York, **1992**, 625–637;
9.   Urum, K., Pekdemir, T., Çopur, M.: Surfactants treatment of crude oil contaminated soils, *Journal of Colloid and Interface Science*, **2004**, <u>276</u>, 456-464;
10.   Redfield, A.C., Ketchum, B.H., Richards, F.A. (Eds.): *The Influence of Organisms on the Composition of Seawater*, The Sea, vol. 2. Wiley, New York, **1963**, 26-77;
11.   Walworth, J.L., Woolard, C.R., Braddock, J.F., Reynolds, C.M.: Enhancement and inhibition of soil petroleum biodegradation through the use of fertilizer nitrogen: an approach to determining optimum levels, *J. Soil Contam.*, **1997**, <u>6</u> (5), 465-480;
12.   AFNOR, recueil des normes français, Qualité des sols, AFNOR Edition, **1994**;
13.   FRENCH INDUSTRIAL STANDARDS AUTHORITY X 31 – 103 (French Industrial Standards Authority; Quality of soils), **1994**;
14.   FRENCH INDUSTRIAL STANDARDS AUTHORITY X 31 – 109 (French Industrial Standards Authority; Quality of soils), **1994**;
15.   Baize, D.: *Guide des analyses courante en pédologie: choix, expression, présentation, interprétation*, INRA, **1990**;
16.   GEPPA: Groupement d'Etudes des Problèmes de Pédologie;
17.   Pansu, M, Gautheyrou, J.: *L'analyse du sol minéralogique, organique et minérale*, Springer, France, Paris, **2003**;
18.   INRA: *Référentiel Pédologique*, Association Française d'Etude de sols, INRA, **1995**;
19.   Cerniglia, C.E.: Fungal metabolism of polycyclic aromatic hydrocarbons: past, present and future applications in bioremediation, *Journal of Industrial Microbiology and Biotechnology*, **1997**, <u>19</u>, 324-333;
20.   Potin, O., Rafin, C., Veignie, E.: Bioremediation of an aged polycyclic aromatic hydrocarbon (PAH)-contaminated soil by filamentous fungi isolated from the soil, *International Biodeterioration and Biodegradation*, **2004**, <u>54</u>, 45-52.