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Turbidimetric Determination of Hydrocarbon Contamination in Passaic River Sediments and Refinery Polluted Soils

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ABSTRACT

A rapid method is described for the determination of petroleum hydrocarbons in soil samples. The method is based on the extraction of hydrocarbons by a solvent and the treatment of the solution with an aqueous solution of a surfactant to release the hydrocarbons to the water phase in the form of a stable emulsion. The emulsion is then utilized to measure the hydrocarbon content by turbidimetry. The effects of various operating parameters including the surfactant solution composition and time of extraction and time of mixing with the releasing solution are investigated. The stability of the emulsion was improved in acid environment containing and electrolyte. The turbidity values (T) were related with hydrocarbon concentration in the extract (C) by the following equation. Turbidity = 2.75 C + 205.7. With R^2 = 0.9929. The soil hydrocarbon content (SHC) measured in µg/g can then be calculated using the formula: SHC = [Extract Vol. (mL) x C]/Sample Wt (g). The results correlated well with the results of total hydrocarbons in soils determined by standard methods. The method was applied for the estimation of hydrocarbons in Passaic river sediments taken from various locations and depths. For field work the method was used to supply data on the hydrocarbon contamination of soil samples taken within an oil refinery and a monitoring well drilled within heavy hydrocarbon waste dumping location.

*Keywords***:** *Hydrocarbon Contamination, Turbidimetry, Refinery Soils, Passaic River Sediments*

1. Introduction

There is an increasing interest in the environmental studies due to the health impacts of the various pollutants. Petroleum hydrocarbons (HC) are among the dangerous materials because they are potential carcinogenic materials. The HC are introduced to our environment from refining and various processes utilizing HC as fuels. On the marine environment they float and prevent the oxygen exchange and reduce the penetration of sunshine from reaching the deep marine phytoplanctons and consequently alter the production of oxygen. Transportation, fallouts and leakage may contribute to the total HC introduction to soil and water. Osuji and Nwoye [1], reported that hydrocarbon pollution of soil generally imply low soil fertility, which in turn implies low agricultural productivity and reduced source of livelihood in the affected area. Thus, contingency/remedial measures should include the application of appropriate and sufficient inorganic NPK fertilizer to restore the carbon to nutrient ratios to the optimum required to stimulate and sustain mi-

crobial activity. Clays like montmorillonite and kaolinite proved capable of promoting microbial growth and allowed microorganisms to proliferate (to a greater degree than in a control sample which contained no clay) in an extremely high concentration of heavy oil [2].

The determination of HC is the first step in the remediation and site assessment programs. Thus, the methods need to be reliable, precise and simple to provide the correct the right data on which the decision makers and engineers make their plans. Systematic methods are available for the detailed and quantitative evaluation of HC contamination levels. The methods involve the extraction of soil samples with organic solvents like dichloromethane or hexane using the soxhlet systems and the concentration of the extract with heating and vacuum to bring the HC concentration up to the detectable levels of the measuring instruments and to recover the solvent. These methods are performed in well equipped laboratories and take more than 24 hrs. Concentrated samples can then be used for quantitative and qualitative evaluations. However, heating and vacuum may result in the loss of

the more important volatile and semivolatile components [3,4].

An impressing approach was introduced by Zhang *et al.* [5], by extracting soil with a water soluble solvent, THF, and followed by turbidimetric determination of the HC after release into water containing surfactant. Based on this procedure patents were registered, namely, US 575635; 5679574 and 6117682 to deal with the determination of petroleum hydrocarbons in water and soil samples. Kulichenko and Shevchenko [6], utilized the Triton X-100-stabilized "oil-in-water" emulsions as suitable media for alkalimetric determination of hydrophobic organic acids. Due to their potent solubilizing and emulsifying properties, synthetic surfactants and biosurfactants can be used for removing hydrophobic pollutants from soil. Pastewski, *et al.* [7], investigated the wetting properties, emulsification and micellar solubilization of non-ionic surfactants and biosurfactant. Emulsions stabilized by Triton X-100 were the most stable.

For field work, a commercial kit was employed for the screening and quantitative assay of petroleum HC in refinery soil samples [8]. The work is based on the extraction of HC with a solvent, filtering with syringe filter and finally adding the filtrate onto a developer to produce emulsion. The emulsion is measured by turbidimetry. The solvent and developer is a property of the manufacturer.

The present paper focuses on the development of solvent surfactant system for the determination of HC in soils. Various operating parameters were evaluated to establish the best conditions for the determination. The method is applied on the determination of HC in Passaic River which is known of its pollution with HC and other contaminants [9] and to soil samples collected from a local refinery in Iraq.

2. Experimental

2.1. Materials and Reagents

Methanol was a spectroscopy grade from Merck. Ethanol was a 95.5% analytical grade reagent from Merck. Triton-X-100 (Merck, AG). The diesel fuel sample used was an Exxon highway diesel fuel with a maximum sulfur content of 15 ppm supplied from a local fuel station in Montclair, NJ.

2.2. Procedures

A stock solution of the low sulfur diesel fuel in methanol-ethanol mixture (3:1 respectively) was prepared by dissolving 2.500 g of the hydrocarbon in the solvent mixture and dilution to 250 mL in a calibrated flask to give a concentration of 10,000 ppm. A set of calibration standards: 50, 100, 200, 300, 500, 750, 1000, 1500 and

2000 mg/L that are equivalent to 0.005, 0.010, 0.020, 0.030, 0.050, 0.075, 0.100, 0.150 and 0.200% were prepared by proper dilution of the stock solution with the solvent mixture. The emulsifier solution was prepared by dissolving 0.250 g of Triton X-100 with 2.5 g of NaCl and 1-mL aliquot of 1 M HCl in the minimum amount of water. The solution was diluted to 250 mL to give 1000 ppm of the detergent in 1% NaCl and (0.001 - 0.002 M HCl. A set of glass bottles were prepared to be used as the reaction cells and a constant volume of the emulsifier solution was introduced to each of them. An aliquot of 5.0 mL of each standard solution was added twice to 10 mLs of the surfactant solution. The mixing time was fixed at 15 s and the settling time at 5 min and the emulsion stabilization at 10 mins. Two readings were taken for each emulsion, *i.e.*, four readings for each standard solution. The turbidity values of the resultant emulsions were measured.

2.2.1. Mixing of Hydrocarbons with water and Emulsification

To a constant volume of water (50 mL) various amounts (10 mL - 50 mL) of the HC alcoholic hydrocarbon solution were added and agitated for 10 s - 60 s. The appearance of the mixture was monitored to ensure the release of HC from the alcoholic solution to water. The immiscibility of HC with water caused the separation of HC as a distinct layer above the water phase. When the best ratio of mixing was evaluated, the experiment was repeated several times to ensure stability and repeatability.

Water in the previous section was replaced with an aqueous solution (1000 mg/L) of the surfactants used. The HC—water mixture will appear as a white translucent (Turbid) solution depending on the amount of the two components. The turbidity measurement this time was employed to detect the release of HC into the water phase.

2.2.2. Calibration Curve

An aliquot of the standard solution was added to the reaction cell t a ratio of 2:3 (HC solution: Detergent solution). The bottle contents were mixed thoroughly for 15 s - 20 s and left to settle for 4 mins. The reaction mixture was poured into the turbidimeter cell and the measurement was taken after 10 s - 20 s.

2.2.3. Synthetic Soil Samples Preparation

Small amount of soil taken from a forest on the surroundings of Montclair city to represent HC free samples was mixed specified volume of alcoholic solution of standard diesel fuel oil. The mixture was thoroughly homogenized to ensure even distribution of the HC in the soil. During homogenization the alcohol was gradually evaporated. Finally the remaining alcohol was evapo-

rated under vacuum. Calculated amounts of the dry HC-polluted soil were place in plastic centrifuge tubes with 10 mL -15 mL of the alcoholic mixed-solvent and the tube was capped. Various shaking time intervals were selected to ensure maximum removal of HC from soil (2 - 10 mins). The mixture was then allowed for enough time for the soil to settle. The extract was decanted into a syringe filter fitted with a 0.2 μm fiber filter. The plunger was fitted to the syringe and pushed to force the clear extract into a vial containing the hydrocarbon-releasing and emulsifying solution. The procedure was completed to develop the formation of emulsion and stabilized for 10 min before the turbidity reading was taken. It appeared that the turbidity values increase as the shaking time increases up till 3.5 min when the reading showed pronounced stability. The shaking time was then fixed on 4-5 min in the proposed procedure.

2.3. Sampling of Sediments and Soils

Several sediment samples were taken from Passaic river sediments at various depths. These samples were studied for their clay contents and total organic matter by Bujalski and Kruge [10] to ensure variety of HC levels and various textures. The samples were also analyzed in accordance with standard EPA method for comparative purposes.

The method was also applied for the estimation of petroleum hydrocarbon contamination of samples taken from a local refinery site including storage tanks, area surrounding the water treatment plant of the refinery and from the heavy hydrocarbons dumping location. Soil samples were also taken during the digging of a monitoring well (8.0 m depth at 0.5 m intervals to evaluate the possibility of penetration of hydrocarbons in the soil and the possible contamination of the ground water. In some cases a small distance between samples gave high differences in the hydrocarbon contents. The choice of these samples was according to the use of the location.

2.4. Determination of Hydrocarbons in Soil

The most relevant sample preparation procedures were applied [11]. Randomly 15 samples from the Daura refinery were selected for the ASTM Soxhlet method. Accurately about 20 g of soil samples were weighed and thoroughly mixed with an equal amount of anhydrous sodium sulfate to aid dehydration and then placed in the extraction cellulosic thimble. The thimble was inserted within the Soxhlet apparatus and hexane (later replaced with dichloromethane) was employed for the extraction. The extraction took 16 hr - 20 hr. In the next day the system was dismantled and the flask containing the hydrocarbon extract was fitted in the RV-05 IKA Rotary Evaporation System to aid the concentration and solvent

recovery. The evaporation continues until the volume of the solution is reduced to 4 mL - 7 mL volume. The concentrate was transferred quantitatively into a watch glass and left for air drying and weighed until a constant weight was obtained.

3. Results and Discussion

3.1. Water-Hydrocarbons Mixing and Emulsification

The addition of the HC alcoholic solution to water resulted in a smoothly separation of HC from the solution. It was found that mixing the solution with water for 15 s - 30 s is adequate for the release of all the HC from the solution to form a distinct layer above the water surface on standing. Thus, the alcoholic mixture acts as a vehicle for the transport of hydrocarbon from the soil into water system. However, beyond 40 mL hydrocarbon solution volume it was clear that not all the HC could be released. By repeating the experiment it was found that a HC solution volume of 20 mL - 30 mL (40% - 60% of water volume) gave the best results. Further, the addition must be done gradually to give the best release of HC.

Hydrocarbons do not mix with water unless an emulsifier is added. The emulsifier is a surface active agent which has two ends of different polarity. The hydrophilic end comprises a hydrolysable group that facilitates intimate mixing with water. The other end is the oleophilic group which dissolves in the oil and hence a total distribution of the HC in the water body. Detergents are used in bulk quantities in the cleaners industry which can successfully separate oil contamination from hands and fabrics by forming micelles giving a stable colloidal solution for a defined time. The HC—water mixture will appear as a white translucent (Turbid) solution depending on the amount of the two components. Ionic and non-ionic detergents are commercially available for the various purposes.

The goal now is to produce an emulsion from the released HC with water and has to be stable for certain interval of time to allow turbidimetric measurement. Household detergent products usually contain some additive like colors and perfumes. Thus, these products could not be employed for the present work. Dodecylbenzenesulfonate, DBS, (anionic detergent) and Triton X-100 (non-ionic detergent) were chosen for this purpose.

The use of DBS 1000 ppm aqueous solution resulted in good emulsion upon mixing but with limited stability (2 min - 4 min). This limited stability will limit the applicability of the resultant emulsion for subsequent turbidity measurements.

Meanwhile, the 1000 ppm triton X-100 solution gave very good emulsion with improved stability of 14 min -

22 min. Thus, the latter was employed for the rest of this study as the emulsifier or the turbidity developing agent. To aid the application, sodium chloride was added to give the required medium for complete rejection of HC into water. The emulsions stabilized by Triton X-100 were the most stable [7]. Acidification was also important because the emulsion breakdown occurs at $10 < pH < 13.5$. An emulsion stability gap was also observed at $10^{-2} < N < 2.5 \times 10^{-1}$ of polyvalent metal chlorides concentration in the initial aqueous phase [12]. However, the addition of inorganic acids did not significantly affect the stability of emulsions stabilized by Triton X-100 [13].

A certain amount of Triton-X100 was found capable of emulsifying a quantity of diesel fuel that is 1.5 times its concentration in water. Also, the presence of the surfactant helps to reduce the mixing time necessary to release the HC into the water phase as it enters directly in emulsion in accordance with Le Chatelier law.

3.2. Determination of Turbidity Reading Time

After the formation of the oil-in-water emulsion at various concentrations, the emulsion was placed in the turbidimeter after ensuring the absence of any air bubbles

and making sure of the cleanliness of the cuvette sides. A solution of moderate hydrocarbon concentration was chosen to evaluate the stability of the emulsion. The emulsion was left for one minute and the turbidity readings started. **Figure 1** shows the development of the reading and its stability over certain time. It appears that the reading was unstable and tends to increase to attain a stable value for another 10 mins. Thus, a time interval of 10 mins must be elapsed before any reliable turbidity reading to be taken for analytical purposes.

3.3. Analysis of Synthetic Samples

The results of the agricultural soil samples contaminated with the diesel fuel oil indicated an increase of the turbidity values with the increase of the shaking time up till 3.5 min when the reading showed pronounced stability. The shaking time was then fixed on 4 min - 5 min in the proposed procedure.

However, the high HC content of the soils is very well reflected by the color of their alcoholic extract being dark brown for the highly concentrated samples. This preliminary observation led to use samples smaller than 10 g for the concentrated soils.
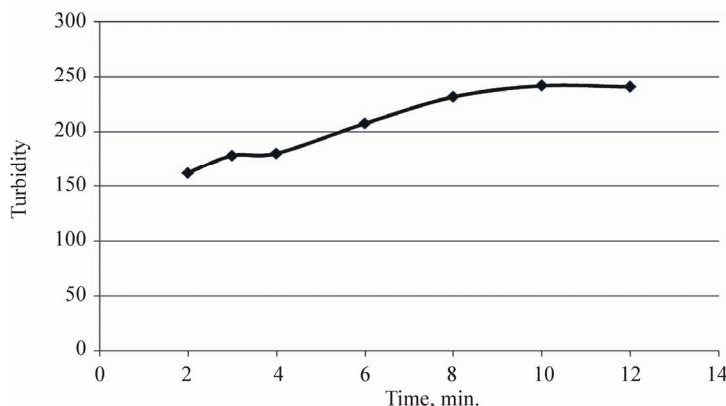

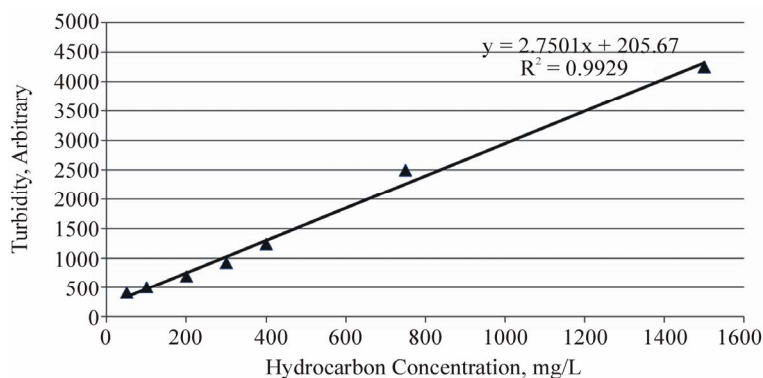**Figure 1. Stability of Turbidity Reading.**

$y = 2.7501x + 205.67$
$R^2 = 0.9929$

Figure 2. Calibration Graph of the Turbidimetric Determination of Hydrocarbons.

3.4. Recommended Procedure

1) In a plastic capped tube, specified amount (2.0 g - 5.0 g) of soil was placed and 10.0 mL of mixed alcohol solvent were added. The tube contents were shaken for 4-5 min and left for 1 min - 2 min to settle.

2) The supernatent solution was decanted into a syringe filter equipped with a 0.2 μm fiber filter. The plunger was introduced into the syringe and the solution was transferred into a 10 mL capped vial.

3) 2.3 ml of the extract was transferred into a small glass bottle of 10 mL - 15 mL size containing the 3.8 mL of the emulsion developing solution. The mixture was shaken for 15 s - 20 s and left for 8 - 12 min to stabilize.

4) The emulsion was placed in the turbidimeter measuring cell and the reading was taken after 10 s - 15 s. Another reading was taken to ensure reproducibility.

5) During the settling time of the extract and the emulsion, other soil sample may be taken and the procedure was applied.

3.5. Range of Application of the Method

For the range of HC concentrations in alcohol only the readings of the two highest standards (1500 and 2000 mg/L) fell out of the range of the turbidimeter. The turbidity values were plotted against the concentration. The signal increased linearly with the increase of concentration (**Figure 3**). Thus, linear correlation expresses the relation of turbidity with concentration over the range of 50 mg/L - 1500 mg/L. However, a power relation was described elsewhere between turbidity and soil hydrocarbon after extraction [14].

Some of the standard solutions were utilized as samples to estimate the HC concentration of HC from the measured Turbidity values. To calculate the HC content of the analyzed soil samples the following relation was employed:

HC% = (Extract Vol * HC concentration)/Soil sample weight, g.

3.6. Applications

The results of HC contents of Passaic river sediments are given in **Table 1** in comparison with some published results [10]. The results correlates well with the total organic contents of Passaic River sediments [9] as can be seen in **Figure 3**. However, the differences may be assigned to the variety of organic materials in the sediment samples including plant residues and others of anthropogenic origin in addition to hydrocarbons [10].

The hydrocarbon contents of some refinery samples determined by the standard Soxhlet gravimetric method were compared with those determined with the present method and the correlation can be seen in **Figure 4**. Reasonable correlation could be attained because almost all light hydrocarbons are already lost from the soil due the long term evaporation during the many years and very hot summer sunshine in Iraq. The appearance of the dried extracts as resinous to greasy materials [8] may account for the significant differences for some samples.

The hydrocarbon contamination distribution in the Daura refinery soils is shown in **Figure 5**. For the soil samples taken during the digging of a monitoring well, the hydrocarbon distribution along the profile of the well can be seen in **Figure 6**. The samples representing the soil within the dumping lagoons, confirmed those related to the soil layers of the monitoring well digging. At a depth of 0.5 m maximum contamination could be observed within the area of the dumping lagoons. The surface soil within the lagoons area is always subject to mixing with clean soil and burning and exposed to the summer sun of Iraq for several seasons. At a depth of 2 m, the soil sample taken within the new project area exhibited almost no hydrocarbon content and very trace-
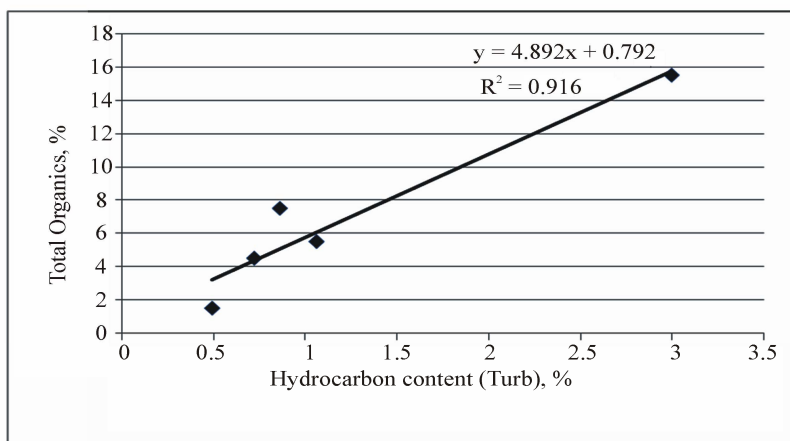

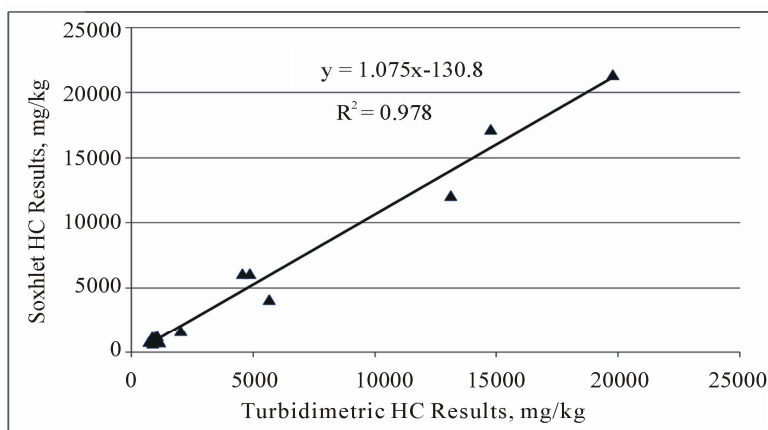**Figure 3. Correlation between Organic Contents and the Turbidimetric Hydrocarbon Results.**

Figure 4. Correlation between Soxhlet and Turbidimetric Hydrocarbon Results or Refinery Soil Samples.
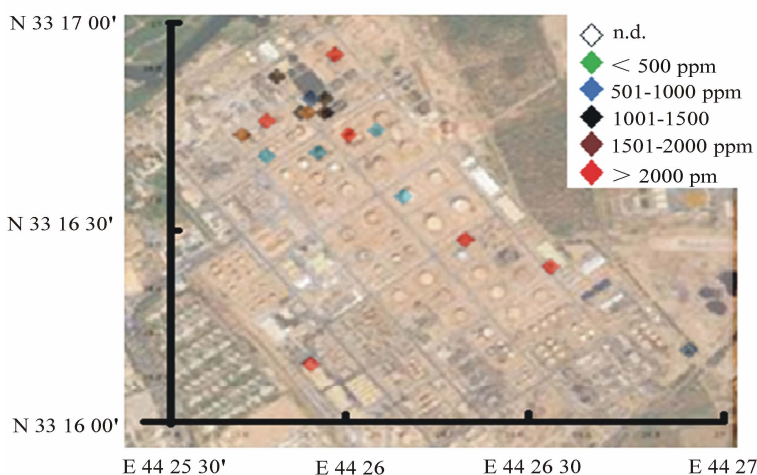

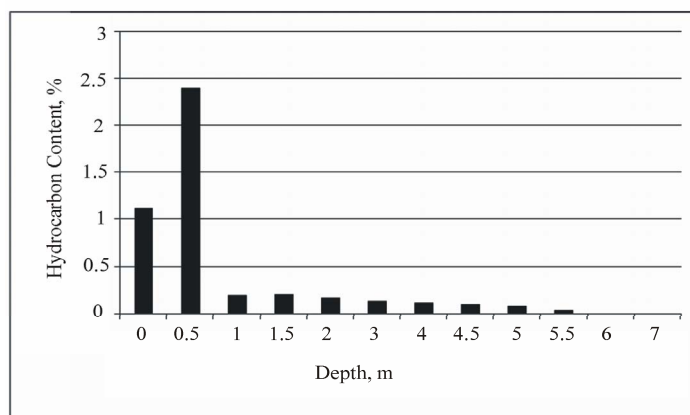**Figure 5. The Distribution of Hydrocarbons within the Refinery Site.**

Figure 6. The hydrocarbon content of the soil of the monitoring well.

amounts of heavy metals. This is related to the difficult penetration of hydrocarbons down to such depths [15]. Some samples were characterized by an average hydro-

carbon content of about 1000 ppm (0.1%). The sample taken at the flare location indicated relatively high hydrocarbon content even at a high dilution.

Table 1. Hydrocarbon Contents of Passaic River Sediment Samples.

Sediment	Turbidity	HC%	Organics % (*)
5A S38	3155	1.06	5.5
5A S46	490	0.49	1.5
7A S34	5318	3.0	15.5
9A S6	2250	0.72	4.5
9A S34	2520	0.86	7.5
10A S28	4320	1.492	---
10A S46	1535	0.495	---

At a depth of 25 cm within the flare area, the hydrocarbon content was less than 0.1%. The area between the ware houses and storage tanks exhibited moderate hydrocarbon content in the soil (0.07%). The samples taken at an average distance of 2 m - 3 m from the area covered by a spill from storage tanks and at certain depths, yet indicated moderate to high hydrocarbon contents (0.08% - 1.48%). The soil at the pipeline between new project and main street (Taken at the storage tanks side) exhibited relatively high hydrocarbon content (>1.5%) indicating the large impact of the storage tanks spills on the pollution of soil. Sample 29 of the area around the TEL tank, exhibited the lowest hydrocarbon content of the soil. This is related to the ignorance of the area for several years period and the role of the metal plate roof of the unit in preventing or making the deposition of hydrocarbons the least in the refinery locations.

The extraction of the soil with methanol and the drying of the solvent at ambient temperature resulted in heavy and highly viscous residue which can be sorted as resinous material. However, the long exposure time of the soil to the heat radiation from the flare and the action of atmospheric oxygen and soil mineral components can account for a catalytic conversion of middle distillates into resinous material [16,17].

The soil contamination with hydrocarbons might have adverse effects on cultivation. However, the wide distribution of the green areas in the site may reflect the utilization of the hydrocarbon contaminants as a source of carbon for the plant growth. Recent studies on the effects of hydrocarbon contamination on the plant ecosystem concluded that more research is required in this area [18].

4. Conclusions

Turbidimetric method for the determination of petroleum hydrocarbons in soil can be a promising technique especially for the field work. The results correlated well with the results of total hydrocarbons in soils determined by standard methods. The method was applied for the estimation of hydrocarbons in Passaic river sediments taken from various locations and depths. For field work the method was used to supply data on the hydrocarbon contamination of soil samples taken within an oil refinery and a monitoring well drilled within heavy hydrocarbon waste dumping location.

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