

# **Photooxidation of Heavy Crude Oil Spilled in Tropical Soil**

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## **Authors' contributions**

*This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.*

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## **ABSTRACT**

Photooxidation was an important weathering process for spilled oil at the on tropical soil following a heavy crude oil spill, leading to the rapid formation of polar or oxygenated hydrocarbons, little is known photo-oxidation of hydrocarbons in soils. This study described the effect of solar radiation on heavy crude oil contaminated tropical soil. Physicochemical parameter of heavy crude oil showed the following values; API was 21.9, which was within the range of heavy crude oil, the density of the heavy crude was 0.8952 g/cm<sup>3</sup>. We examined the effect of ultraviolet light on crude oil using gas chromatography method for day 0, 14, 28 and 42. The results show a remarkable reduction in the total petroleum hydrocarbon [4664.56 mg/l to 1548.85 mg/kg] and poly aromatic hydrocarbon content of heavy crude oil [37.44 mg/kg to 2.12 mg/kg] from day zero to day 42. The saturated compounds was resistant, but the aromatic compounds were particularly sensitive to photo oxidation. This study provides quantitative measures of oil degradation under relevant field conditions, and improves our understanding of the role of sunlight on the fate of spilled oil on natural soil biota.

**Keywords:** *Photo oxidation; fate; tropical soil; degradation; solar radiation; ultraviolet light.*

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## 1. INTRODUCTION

Photo oxidation is a family of light-catalyzed reactions that oxidize the reduced carbon in petroleum hydrocarbons. It also plays an important role in the removal of volatile petroleum hydrocarbons and this was shown in studies of the *exxon valdez* where as much as 70 % of the crude was found to be photooxidized in the water or in the atmosphere [1,2]. The necessary ingredients for photo oxidation are radiation and light-absorbing molecules (chromospheres). It is a potentially significant process in the degradation of crude oil spilled on tropical soil. When crude oil is spilled on land, it undergoes a series of weathering processes, including evaporation, biodegradation, and photo oxidation [3,4]. Some of these processes transpose oil, whereas some alter it., evaporation transfer oil between soil column and air respectively, but they do not alter the chemical composition of low molecular weight hydrocarbons compounds in oil. In contrast, photo oxidation and biodegradation are transformative: it adds oxygen to components in the oil, creating new compounds with different properties than those initially in the spilled oil. Thus, the effect of photo oxidation is distinctly different from that of biodegradation, where larger and more substituted compounds are more resistant to degradation. Polycyclic aromatic hydrocarbons were found to be more susceptible to photooxidation as a removal or transformation process, whereas the weathering of n-alkanes and lower molecular weight organic compounds was found to be driven more by biodegradation processes [5,6].

Photo-oxidation, a vital process in the weathering of oil [3], produces a variety of oxidized compounds, including aliphatic and aromatic ketones, aldehydes, carboxylic acids, fatty acids, esters, epoxides, sulfoxides, sulfones, phenols, anhydrides, quinones and aliphatic and aromatic alcohols. Some of these compounds contribute to the terrestrial biota toxicity observed after an oil spill [7]. Photooxidation is an important phenomenon not because it removes large volumes of oil from the environment but because it removes the molecules of most toxicological concern [8].

Photooxidation can occur direct, when reactants absorb natural sunlight energy, to form a less stable intermediate, such as poly aromatic hydrocarbon are oxidized. A compound that absorbs light energy and as a result, its chemical

structure altered, undergoes direct photolysis. Chromophores such as alkenes or aromatic rings, with unsaturated carbon/carbon bonds or fatty acids with carbonyl groups, as well as nitrosamines, benzidines, chlorinated organics and some metal complexes are susceptible to direct photolysis [9]. This process is limited to the tiny fraction of oil components that absorbs sunlight [10]. Indirect photo oxidation is when other species in the in crude oil absorbs sunlight, another compound present in the environment, namely the photosensitizer (e.g., quinones, humic acid, flavins, as well as trace metals, nitrate, nitrite, and hydrogen peroxide) absorbs light energy and then transfers it either indirectly via various reactive intermediates such as oxidants or directly to the compound of interest causing its structural alteration [11]. A wide range of reactive oxygen species are produced, including singlet oxygen, peroxy radicals, and hydroxyl radicals. Increase in oxygenated hydrocarbons may be more susceptible for biodegradation. In addition, many dyes, pigments and aromatic hydrocarbons may act as sensitizers [12]. Compounds unable to undergo direct photolysis due to the absence of chromophores in their molecules may be photolyzed indirectly via sensitized photolysis or photo-oxidation. These species can oxidize other compounds in oil, not just those that absorb light directly. Thus, indirect photooxidation produces, a much larger fraction of spilled oil would be vulnerable to oxidation because few petroleum hydrocarbons absorb sunlight efficiently. It has been proposed that photooxidation could be an effective attenuation mechanism for heavy hydrocarbons [13] less is known about the importance of photo-oxidation of hydrocarbons in soils. As the process requires direct sunlight it will be effective only at the soil surface. Garret et al., [3] understanding the effect of photochemical degradation on crude oil is a prerequisite for providing an accurate description of the recent history and potential fate of oil spilled in a terrestrial environment [14].

## 2. MATERIALS AND METHODS

### 2.1 Experimental Set Up

Ex-situ techniques were employed for this study. Soil sample was packed in a glass sheet of rectangular shape (100 cm × 50 cm × 50 cm) according to soil profiling, with leachate collection system. A large cylindrical tube was rolled over the surface to make flat and smooth while filling it with soil until the soil surface was even with the

container edge. This was kept for four months allow the soil particles settle [from January to April]. A mixture of 20,000 ml (20 litres) heavy crude oil was poured onto the surface of the soil through a funnel and allowed to begin spreading and infiltration on the soil surface.

## 2.2 Sample Collection

Polluted soil was collected with soil auger into polyethylene bags sterilized with 70% ethanol from the crude oil polluted site at the depth (0-0.5m) periodically at 5 different points at the day zero of the spill. Subsequent sample collection was done on day 14, 28 and 42. All samples were transported to the laboratory within 6h at 4°C for analyses.

## 2.3 Physicochemical Analyses of Heavy Crude Oil

The following physicochemical analyses of heavy crude oil spilled parameters were determined; hydrogen sulphide content, specific gravity, water content, API, ignition temperature, density, pour point, salt content, Polyaromatic hydrocarbon, Total Petroleum Hydrocarbon. This was done according to method described by APHA (1998).

## 2.4 Gas Chromatography (GC) Analysis

Analysis of the spilled soil by GC/MS basically followed by the procedure of [15]. the analyses of soil contaminated with heavy crude oil was performed on a Thermo finnigane GC 2000 equipped to trace ms. the following chromatographic conditions were used: 60m x 0.25 mm hp-5 fused silica capillary column. Helium was used as the carrier gas at a flow rate of 1ml/min. the column temperature was set to 70°C for the first 4min, increased 5°C/min to a temperature of 295°C and maintained at 295°C for 30 min.

## 3. RESULTS AND DISCUSSION

Table 1 shows the characteristics of the Heavy crude oil used in this study. It had an API of 21.9 which corresponds with the range for heavy crude oil. Specific gravity of 0.8953, density of 0.8952 g/cm<sup>3</sup> and Water content of 0.18. The heavy crude was exposed to ultraviolet light and analyzed by gas chromatography to identify the components of the crude oil that are most susceptible to photo oxidation. This was to generate an easily measurable effect on the oil, thus, conditions were designed to yield a high



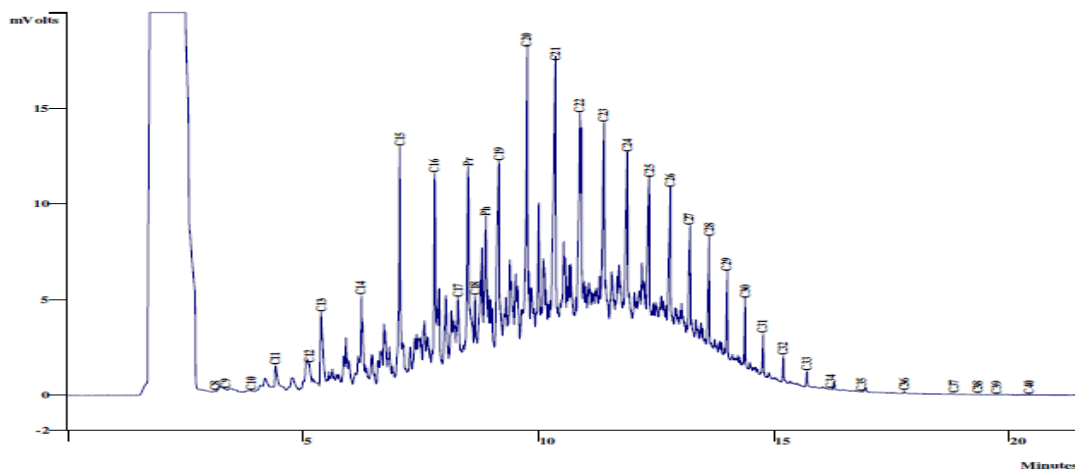
Plate 1. A graduated glass sheet of rectangular shape of soil profile (100 cm x 50 cm x 50 cm)

**Table 1. Baseline properties/ characterization of Heavy Crude oil Sample**

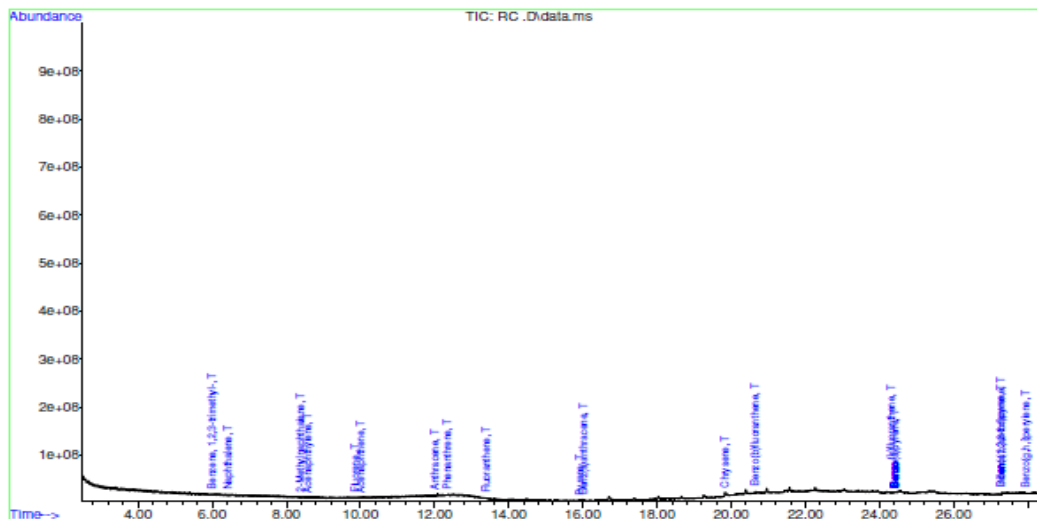
Parameters	Analysis of heavy crude oil
Specific gravity	0.8953
Density.g/cm <sup>3</sup>	0.8952
API °	21.9
Water content mg/l	0.18
Pour point, °C	11.37
Salt Content, mg/l	0.11
Ignition Temperature, °C	48.40
Hydrogen Sulphide	<0.01`

degree of photo oxidation. At the point of exposure (day zero), the oil was extracted and concentrated for analysis using gas chromatography method this showed a total petroleum hydrocarbon to be of 4664.56mg/kg

[Fig. 1]. Hydrocarbon loss was observed on day 14 exposure to be 2068.88 mg/kg [Fig. 3] and 1877.37 mg/kg concentration of the heavy crude oil reduction was observed in day 28 exposure [Fig 5]. 1548.85 mg/kg reduction in the



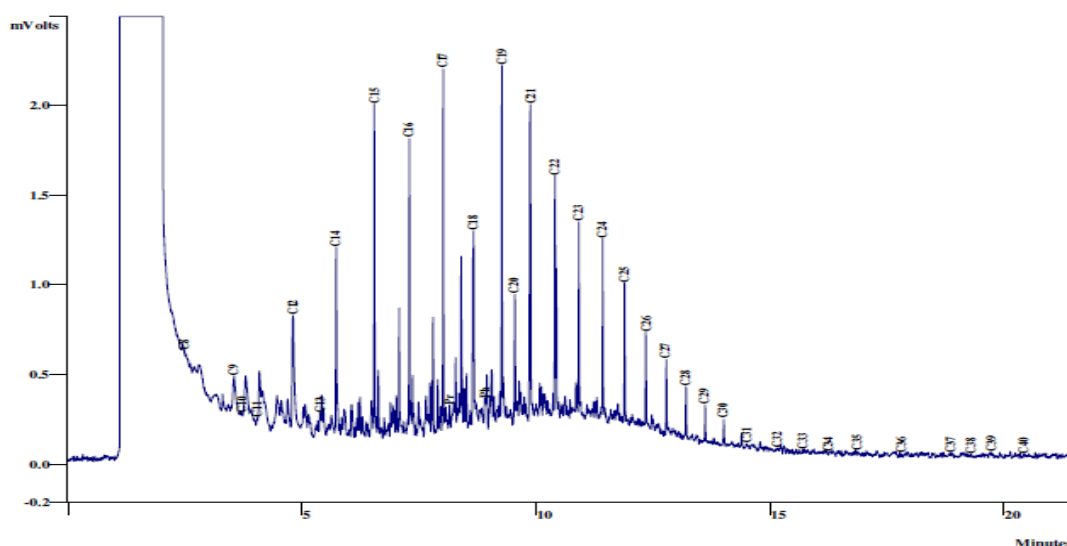
**Fig. 1. Chromatogram of the total petroleum hydrocarbon content in soil sample (TPH: 4664.5638 mg/l [Day zero])**



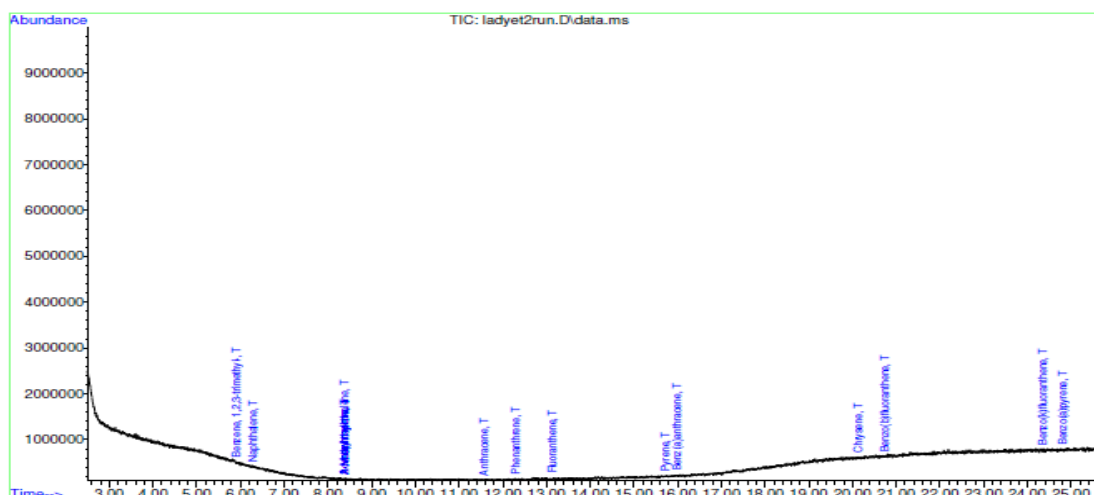
**Fig. 2. Chromatogram of the polyaromatic hydrocarbon content in soil sample (PAH 37.44ppm day zero)**

concentration of the heavy crude oil was observed in day 42 [Fig 7] Also, there was a substantial decline in the poly aromatic fraction of the heavy crude oil from day zero which was 37.44 mg/kg [Fig 2], 13.44 mg/kg on day 14, 2.47 mg/kg on day 28 which was and 2.12 mg/kg on day 42 caused by solar radiation. This corresponds with the work done by Maki *et al.*, 2001 that there was a remarkable change in the aromatic fraction of the crude oil when exposed to sunlight. The summary of the total hydrocarbon loss was represented in Fig. 9 and 10. The graph showed that photooxidation on day 0 to 14

was rapid as the aromatic fraction leaves the heavy crude oil, the rate of reduced from day 28 to 42. All the compounds were decomposed, but the rates of this photodecomposition was very different from one another [Fig. 11] Of these aromatic hydrocarbons, anthracene, phenanthrene, and 1,2-benzanthracene were well-decomposed in comparison with the others, and the sulfur-including heteroaromatic compounds show the same degree of decomposition as compounds with an anthracene ring.



**Fig. 3. Chromatogram of the TPH content in crude oil polluted soil sample (TPH: 2068.8801 mg/kg) day 14**



**Fig. 4. Chromatogram of the PAH content in crude oil polluted soil sample. (PAH: 13.88 mg/kg) [Day 14]**

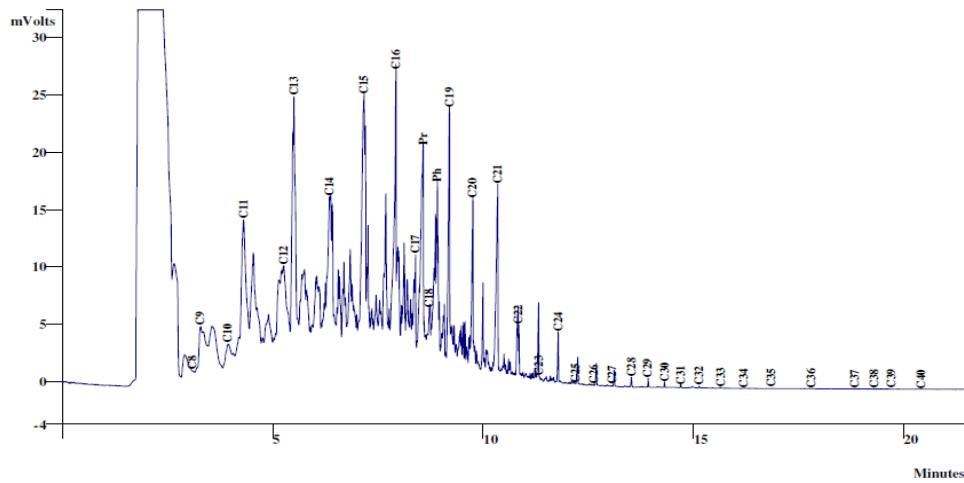


Fig. 5. Chromatogram of the TPH content in crude oil polluted soil sample. (TPH: 1877.3674 mg/kg) Day 28

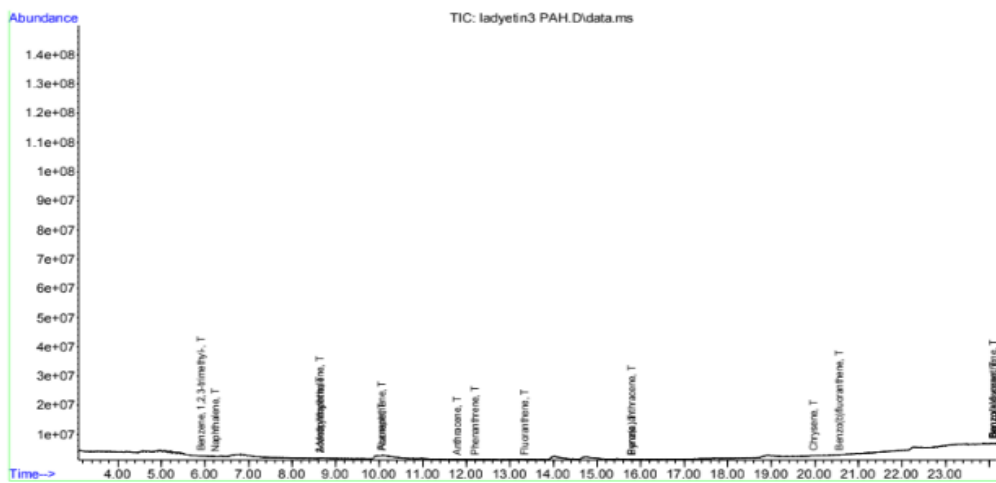


Fig. 6. Chromatogram of the PAH content in crude oil polluted soil sample. (PAH:2.47mg/kg) [Day 28]

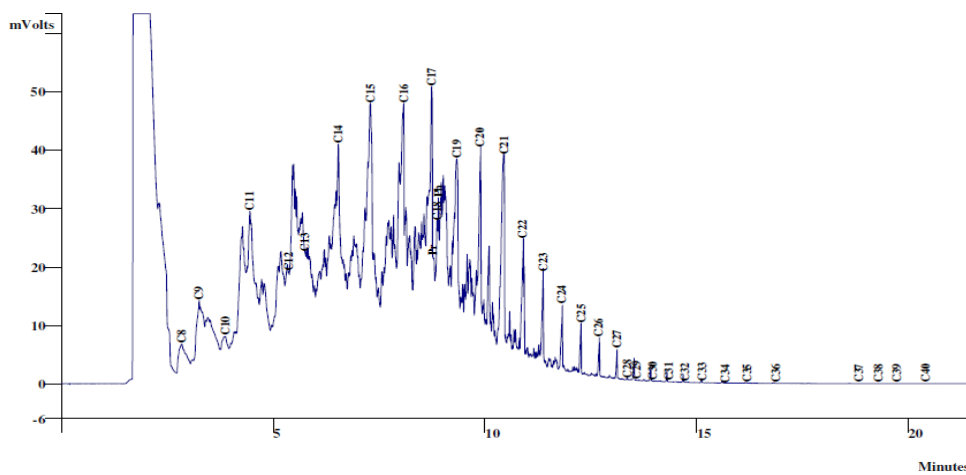


Fig. 7. Chromatogram of the TPH content in crude oil polluted soil sample (TPH: 1548.8524 mg/kg) day 42

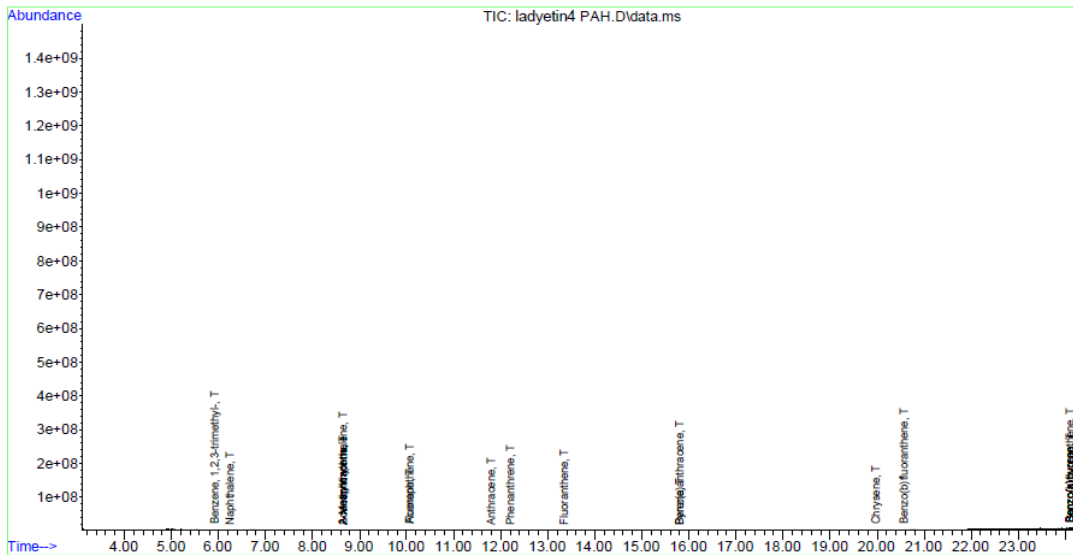


Fig. 8. Chromatogram of the PAH content in crude oil polluted soil sample (PAH:2.12mg/kg) [day 42]

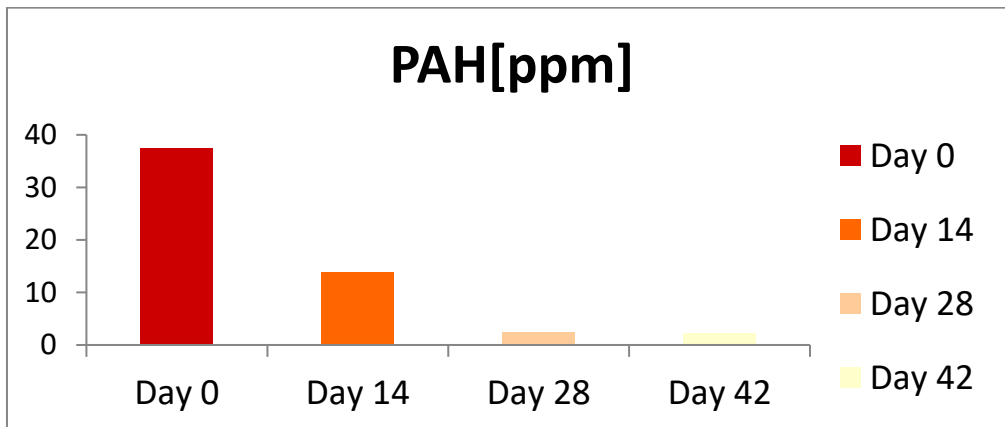


Fig. 9. Total Petroleum Hydrocarbon loss in heavy crude oil contaminated soil [Day 0 to day 42]

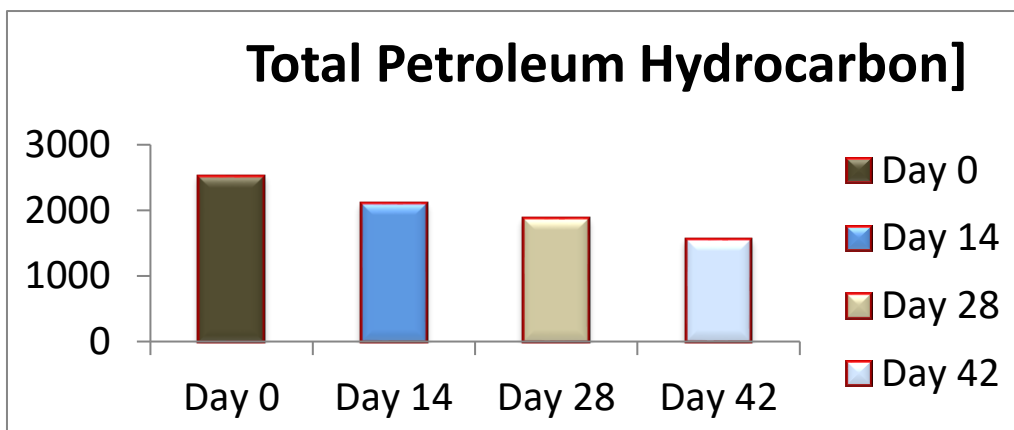


Fig. 10. Poly aromatic hydrocarbon loss in heavy crude oil contaminated soil [Day 0 to day 42]

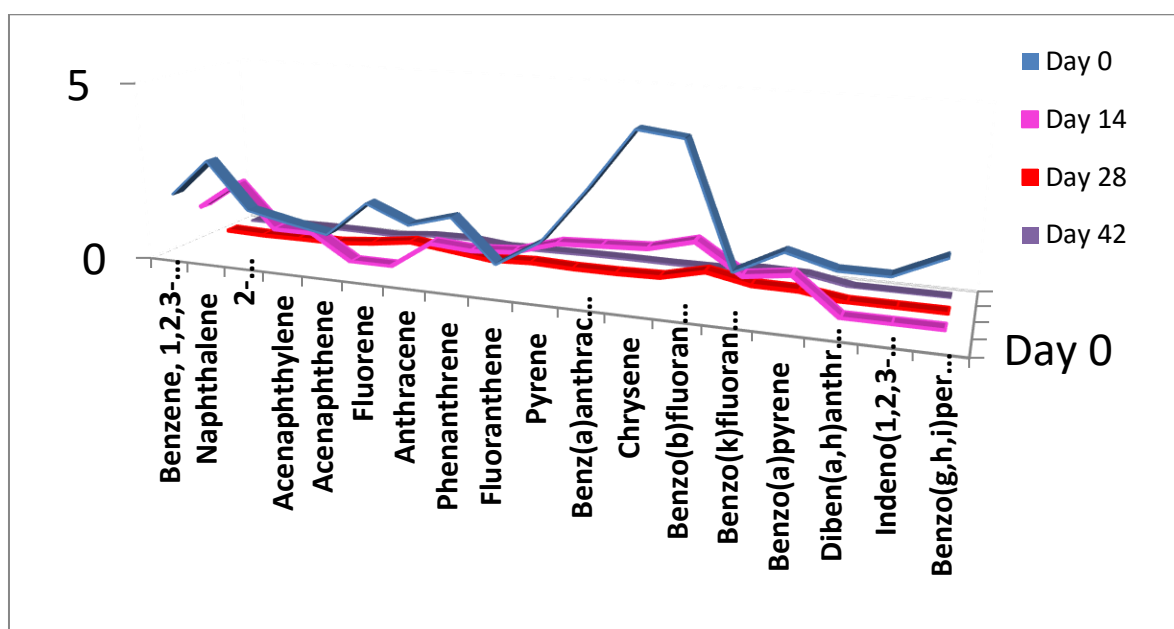


Fig. 11. Photo oxidation of target compounds polyaromatic compounds [PAH] from heavy crude oil spillage

#### 4. CONCLUSION

Photooxidation plays an important role in the removal of volatile petroleum hydrocarbons. This study shows a significant reduction the aromatic fraction of the heavy crude oil spilled in tropical soil which is important in biodegradation studies.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

#### REFERENCES

- Richard L. Photo-oxidation and photo toxicity of crude and refined oil spill. *Spill Science and Technology. Bulletin.* 2003; 8(2):157-162.
- Prince RC, Garrett RM, Bare RE, Grossman MJ, Townsend T, Sufliita JM, et al. The roles of photo oxidation and biodegradation in long term weathering of crude and heavy fuel oils. *Spill science and Technology. Bulletin.* 2003;8:145-156.
- Garrett RM, Ingrid JP, Copper EH. Photo oxidation of crude oils, *Environmental. Science. Technology.* 1998;32:3,719–3,723.
- Braddock JF, Lindstrom JE, Prince RC. Weathering of subarctic oil spill over 25 years. The caribou-poker creeks research water shed experiment. *Cold Regions Science and Technology.* 2003;36:11-23.
- Bacosa HP, Erdner DL, Liu Z. Differentiating the roles of photooxidation and biodegradation in the weathering of Light Louisiana Sweet crude oil in surface water from the Deepwater Horizon site. *Marine. Pollution. Bulletin.* 2015;5:265–272.
- Overton EB, Wade TL, Radovic JR, Meyer BM, Miles MS, Larter SR. Chemical composition of Macondo and other crude oils and compositional alterations during oil spill. *Oceanography.* 2016;29(3):50-63.
- Ward C, Armstrong C, Conmy R, French-McCay D, Reddy M. Photochemical Oxidation of Oil Reduced the Effectiveness of Aerial Dispersants Applied in Response to the Deepwater Horizon Spill. *Environmental Science & Technology Letters.* 2018;5:5,226-231
- Aeppli C, Carmichael CA, Nelson RK, Lemkau KL, Graham WM, Redmond MC, et al. Oil weathering after the Deepwater Horizon disaster led to the formation of oxygenated residues, *Environmental. Science. Technology.* 2012;46(8):799–8,807.
- Snyder K, Mladenov N, Richardot W, Dodder N, Nour A, Campbell C, Hoh E. Persistence and photochemical transformation of water soluble constituents from industrial crude oil and natural seep oil



- in seawater. *Marine Pollution Bulletin*. 2021; 165:112049.
10. Shankar R, Shim WJ, An JA, Yim H. A practical review on photo oxidation of crude oil: laboratory lamp setup and factors affecting it. *Water Research*. 2015; 68:304-315.
  11. Wang Q, Leonce B, Seeley ME, Adegboyega N, Lu K, Hockaday W, Zhanfei L. Elucidating the formation pathway of photo-generated asphaltenes from light Louisiana sweet crude oil after exposure to natural sunlight in the Gulf of Mexico. *Organic Geochemistry*. 2020;150: 104126.
  12. Maki H, Sasaki T, Harayama S. Photo oxidation of biodegraded crude oil and toxicity of photooxidized products. *Chemosphere*. 2001;44(5):1145-51.
  13. Prince RC, Lessard RR. Crude oil releases to the environment: Natural fate and remediation options. *Encyclopedia of Energy*. 2004;1:727-736.
  14. Hall GJ, Frysinger GS, Aeppli C, Carmichael CA, Gros J, Lemkau KL, et al. Oxygenated weathering products of Deepwater Horizon oil come from surprising precursors. Oxygenated weathering products of Deepwater Horizon oil come from surprising precursors, *Marine Pollution Bulletin*. 2013;75:140–149.
  15. Ganjali ST, Niknafs BN, Khosravi M. Photooxidation of crude petroleum maltenic fraction in natural simulated conditions and structural elucidation of photoproducts. *Iran. Journal Environmental Science: Health. Science Engineering*. 2007;4(1):37-42.

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