

# Polyaromatic Hydrocarbons and Metals in Soil Contaminated with Spent Oil Found at Automobile Workshops in Akure, Nigeria

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## Abstract

Soil samples from different automobile workshops and one control sample obtained from a residential area in Akure, Nigeria were quantified for heavy metals and polycyclic aromatic hydrocarbon. The heavy metals analyzed in all samples were Lead (Pb), Cadmium (Cd), Nickel (Ni), Manganese (Mn), Chromium (Cr), Zinc (Zn) and Copper (Cu). Cadmium (Cd) was obtained was below the level of detection in all samples. Manganese was found to have the highest concentration in all samples with concentration of 614.00mg/kg, 560.00mg/kg and 199.00mg/kg with government accredited site having the highest of 614.00mg/kg and the control sample with the lowest concentration of 199.00mg/kg. The concentration of Ni was found to have the lowest value which is 9.00mg/kg, 7.07mg/kg and 2.90mg/kg in all sites when compared with other heavy metals. Control Sample has the lowest concentration for Pb, Ni, Mn and Cu except for Zn which is of the same concentration with an automobile workshop own by an individual. Eight (8) polycyclic aromatic compound which are cyclohexane, (1, 2, 2,-tri fluorine, anthracene, phenanthrene, fluoranthene, pyrene, benz (a) anthracene, were found in all soil samples.

## Keywords

Pyrolytic Process, Pollutants, Carcinogenic, Automobile Workshop

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## 1. Introduction

Polyaromatic hydrocarbons (PAH) are pollutants that are detrimental to the environment when they exceed the permissible level. They are natural pollutants in the environment that are commonly formed in combustion processes of carbonaceous substances at slight or high temperatures and are found in soil, sediments, water and air [1]. Polycyclic aromatic hydrocarbons (PAHs) contain chemical compounds that consist of carbon and hydrogen with a fused ring structure, containing a minimum benzene ring [2]. Polyaromatic Hydrocarbons were documented for their toxicity. [3] and their mutagenic or carcinogenic

properties are the main risk to human health [4].

Theoretically, PAHs could have infinite benzene rings and the arrangement of those benzene rings could produce a copious number of isomers. However, PAHs most studied include 8 or fewer rings, with the maximum environmentally sizeable ones having seven or much less [5].

In PAHs, straight-chained hydrocarbons may also be attached to the rings at one or more points [6]. They form homologous series containing a non-alkylated that is PAH known exist as the parent compound and alkylated PAHs that have the parent compound as the base.

PAHs attached by one alkyl chain are classified as C-1

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members, those with two alkyl chains are classified as

C-2 members and those with three alkyl chains are C-3 members and so on. Commonly associated with PAHs are heterocyclic, compounds in which an atom of nitrogen, sulphur or oxygen has replaced one carbon atom in a ring [6]. These compounds result from pyrolytic processes and the incomplete combustion of organic matter at high temperatures, and anthropogenic activities are the main source of poly hydrocarbons in the environment. In related to their adverse effect on health, their persistence in the environmental matrices and their reactivity and ability to transform into more active species, PAHs have been classified as priority pollutants by the European Environment Agency (1999). Polycyclic aromatic hydrocarbons are persistent in the environment because of their relative chemical stability and resistance to biodegradation. Previous work had shown that exposure of human body to the environment containing PAHs induce some fatal diseases respiratory and excretory organs [8].

PAHs are more soluble in oil than water, this property serves as an advantage for their presence in soils, sediments, and oily substances. It is a common sight to see burnt wood and fuel-related products in the metropolis. People unknowingly cultivate and produce food from the soils that are affected by polycyclic aromatic hydrocarbons [9]. The sources, natural and mostly anthropogenic of PAH in the environment are numerous and include burning of sewage and release of automobile exhaust into the environment, activities of industrial plants, etc. Soil contamination and pollution arises in the environment principally as the result of anthropogenic activities. The direct discharge of industrial wastes to soil, the accidental spillages of chemicals, the application of agricultural chemicals (pesticides) to soils, the percolation of contaminated surface water to subsurface stratum or improper disposal of wastes (*e.g.* leaching of wastes from landfills) are just a few examples causing soil pollution with a variety of inorganic and organic pollutants [10]. On the contrary, if the pollutants are spread in the environment, or the pollution is of a general nature and cannot be traced to a single source, it is called diffuse pollution [6]. The nature and degree of pollution for each polluted site vary widely, but in most cases, polluted sites do not create immediate dangers and serious risks to the surrounding population. Instead, associated risks to polluted sites are generally those resulting from exposure to pollutants at low doses over a long period of time, which may even correspond to a lifetime.

Spent Engine oil sometimes referred to as waste engine oil is produced from automobile mechanic shops and mechanical or electrical repairer shops [13]. The produced oil had been

found to cause great damage and significant chemical changes to environment and create risks of contamination to soil which pose danger to both biotic and abiotic life. Due to the diffuse and nature of petroleum hydrocarbons and heavy metals in Nigeria polluted sites. The frequent pollution of the soil with used engine usually influence the quality and functional properties of the soil whereby its importance to support life reduces such that its quality parameters, etc become impaired [14, 15], the present study is centered on soil polluted by spent engine oil which is predicted to be rich with heavy metals as the heavy metals are found in the environment as results of anthropogenic activities, mainly related to energy and mineral consumption. Common sources of heavy metals include mining, industrial and municipal wastes, motor vehicle emissions, lead-acid batteries, fertilizers, pesticides, and all sewage-derived materials [15, 17] Exposition to heavy metals may occur in several ways by oral, dermal or inhalation route. For instance, drinking water sources can be polluted by heavy metals. Moreover, plants growing on heavy metal polluted soil or exposed to heavy metals through the uptake of polluted water may result contaminated, endangering the food chain. Likewise, absorption through skin owing to direct contact with polluted soil is another potential source of heavy metal exposition. Motor vehicle emissions are a major source of airborne contaminants as well. As heavy metals are hard to metabolize they accumulate in living organisms causing detrimental effects. The toxicity exerted by heavy metals is mostly the result of the interaction with biomolecules (*e.g.* proteins, enzymes, nucleic acids) interfering with their normal functioning. Exposure to heavy metals can have carcinogenic, nervous system, immune system and circulatory effects [18].

There are several chronic diseases associated with delay exposure of heavy metal which include and not limited to mental lapse, kidney toxicity, liver enlargement and infection related to the gastrointestinal tract. Arsenic causes dermal poisoning and has very harmful effects on kidneys and the central nervous system [19]. The previous research had shown that there is a link between accumulation of copper and decline of intelligence quotients in young adolescents [20].

## 2. Materials and Methods

### 2.1. The Study Area

The study areas were two (2) automobile workshops in Akure Metropolis and one control sample from residential area, Ondo State; Nigeria. One of the workshops was designated as government accredited site for Akure automobile workshop and this has made the site to be the busiest in the town.

## 2.2. Reagents and Standards

All reagents used were of chromatographic and analytical grade which are traceable to National Institute of Science Technology. These include anhydrous sodium sulfate, Dichloromethane (DCM), Methanol, Nitric acid, n-Hexane, Laboratory Ultra-pure water was purchased from Matador Dafon Pharmaceuticals Ltd, Akure, Ondo State-Nigeria. Standard Solution for Atomic Absorption Spectrophotometer purchased from Buck Scientific, USA. All glass wares were carefully washed and rinsed with acid solvent (2M HCL) before use.

### 2.2.1. Sample Digestion and Heavy Metals Determination

2g of the sample were weighed into a digesting tube and 10ml of mixture of concentrated nitric acid and concentrated hydrochloric acid;(1:3) (aqua regia) were added and placed in a microwave digester at 700°C for 3hours and monitored until the fume of nitric acid ceased and a clear solution obtained. The digests obtained were made up with Distilled Deionized water in a 100ml standard flask which was later transferred into a well cleaned and pre rinsed sample bottle for heavy metal analysis. The digest obtained was analyzed for different heavy metals using Buck Scientific Atomic Absorption Spectrophotometer VGP210 at Central Research Laboratory of The Federal University of Technology, Akure-Nigeria.

### 2.2.2. Extraction and Gc-Ms Analysis

Extraction of hydrocarbon was done in a sonicator (Grant XUB 18 Ultrasonicator) available at Central Research Laboratory, Federal University of Technology, Akure. 10g of sample was extracted using 50:50 mixture of n-Hexane and Dichloromethane. The mixture was placed in the sonicator with degasser and left there for 8hours in other for the extraction to complete. The cleanup was done using C18 SPE cartridges, Dichloromethane (5ml) and 20ml of n-Hexane, a ratio of 1:4 at elution rate of 1mL/min in sequence were allowed to run through the SPE cartridges. The 1:4 mixture was allowed to drop to the level of the SPE column. The extract was loaded on each column and eluted at 1mL/min. The SPE columns were drained with 20mL n Hexane. The eluent obtained were concentrated under the flux of nitrogen gas and the concentrate transferred into 2mL amber vial bottles. Samples were analyzed using Gas Chromatographic system installed with auto-sampler with helium carrier gas and a quadrupole Mass Spectrometer (Agilent 5975 MSD). The following conditions were also set up: Oven program 65°C (0.5min) to 220°C at (15min.) @4°C/min. Injector temp.: 320°C, Detector temp.: 330°C, Carrier: Helium,

constant flow @2.0mls/min., 1µL Splitless injection, Purge time: 1.75min. @75mls/min and Agilent J&W DB-5ms UI, 20m×0.18, 0.18µm. Poly aromatic hydrocarbons present were quantify using mixed standard of polyaromatic hydrocarbon obtained from Accustandard Inc.

## 3. Results and Discussion

The volume of activities at the workshops implies to have a direct relationship with the concentration of heavy metals on the site. From the results obtained in Table 1 it is shown that the government accredited site which accommodates several individual workshops had the highest concentration of heavy metals except for Lead (Pb) and Copper (Cu) which is higher in workshop owns by an individual. There is a variation between the control sample and other samples for all elements analyzed except for Zinc (Zn) which have the same concentration as that of government accredited sample.

The results obtained for Cadmium (Cd) as shown in table 1 was found to be below the detection limit as shown in table 3 which agreed with the result previously obtained in the analysis of soil in Akure as reported by [16].

All heavy metals analyzed are found to be below the maximum permissible level in soil as presented in table 3 and established by World Health Organization (WHO), Food and Agriculture Organization (FAO) and Ewersls Standard Guidelines in Europe and reported by Chroma *et al.* (2014).

The soil obtained from the government accredited automobile workshop was found to contain Ten Polycyclic Aromatic Hydrocarbon as shown in table 2 and figures 1 to 3 which is the chromatogram obtained and table 2 showed that Benzene (a) anthracene having the highest peak height and percentage area of 960880 and 13.33% respectively followed by Benzo (a) pyrene having peak area and percentage area of 887745 and 12.32 respectively and the trend for others is as follows: Benz (a) anthracene > Benzo (e) pyrene > Pyrene > Fluoranthene > Benz (e) acephenanthrylene > Phenanthrene > Anthracene > Fluorene.

## 4. Conclusion

The study revealed a direct relationship between the activities of automobile technicians on the site and the soil which may influence the quality and safeness of the soil in its use for agricultural purposes. The long time effect of these activities may include the exposure of the soil to higher concentration of heavy metals which may have an adverse toxic effect on the environment and may cause gene mutagenicity in human.

**Table 1.** Reveals the mean concentration of Heavy Metals present in the three sites (mg/kg).

| Sample | Pb          | Cd | Ni        | Mn          | Cr         | Zn         | Cu         |
|--------|-------------|----|-----------|-------------|------------|------------|------------|
| A      | 47.97±0.06  | ND | 9.00±0.01 | 614.67±1.47 | 32.00±0.09 | 32.00±0.00 | 48.00±0.03 |
| B      | 438.17±0.76 | ND | 7.07±0.12 | 560.00±0.58 | 13.33±0.33 | 13.03±0.06 | 77.00±0.00 |
| C      | 0.25±0.03   | ND | 2.90±0.06 | 199.00±0.40 | 18.00±0.02 | 32.00±0.04 | 6.00±0.01  |

\* ND: Below the Detection Limit.

\*Sample A is government accredited automobile workshop site, Sample B is an individual own automobile workshop and Sample C is control sample obtained from residential area.

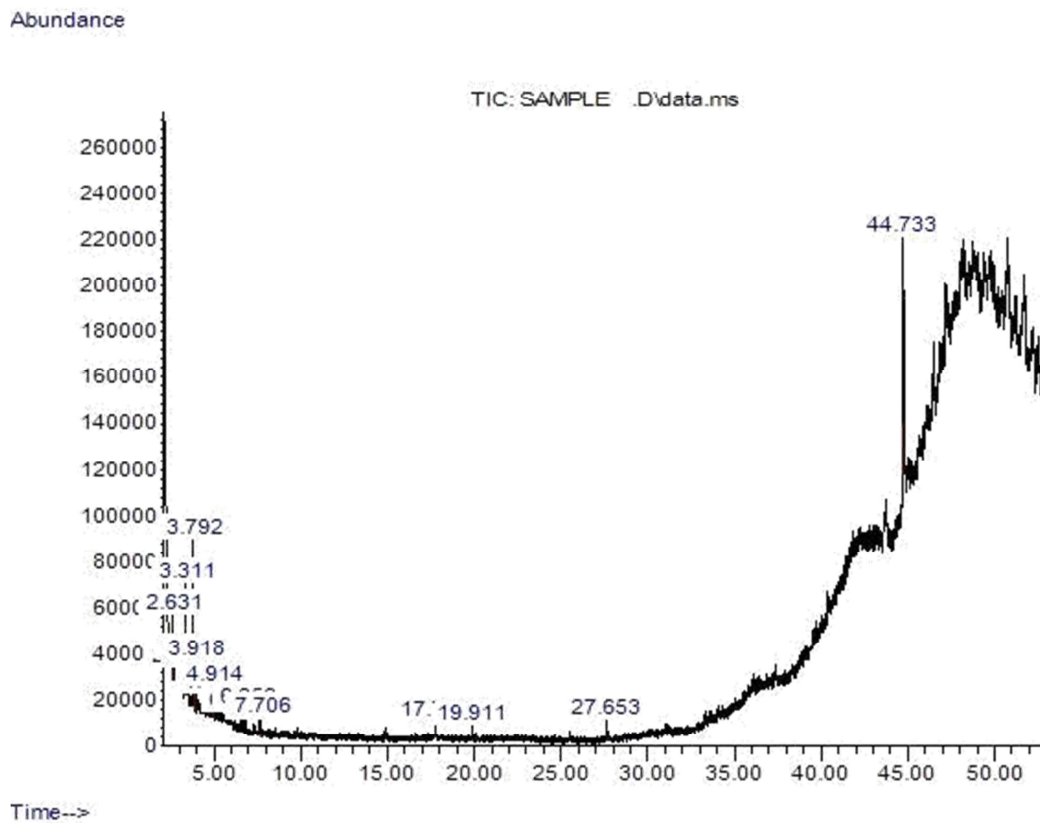
**Table 2.** Shows the Result obtained using GC-MS for quantification of polyaromatic hydrocarbon.

| Compound                   | Concentration | A Concentration B | Concentration C |
|----------------------------|---------------|-------------------|-----------------|
|                            | µg/mL         | µg/mL             | µg/mL           |
| Cyclohexane, (1, 2, 2-tri) | 306.18        | 193.88            | 541.96          |
| Fluorene                   | 2.51          | 2.50              | 5.54            |
| Anthracene                 | 1.56          | 2.04              | 2.17            |
| Phenanthrene               | 5.15          | 5.30              | 5.16            |
| Fluoranthene               | 2.12          | 3.89              | 3.23            |
| Pyrene                     | 2.09          | 4.84              | 6.05            |
| Triphenylene               | ND            | ND                | ND              |
| Benz (a) anthracene        | ND            | ND                | ND              |

**Table 3.** Shows the permissible level in mg/kg for heavy metals in soil.

| Heavy Metals | Maximum permissible level in soil |
|--------------|-----------------------------------|
| Cd           | 3.00                              |
| Cr           | 100.00                            |
| Cu           | 100.00                            |
| Mn           | 2000.00                           |
| Ni           | 50.00                             |
| Pb           | 100.00                            |
| Zn           | 300.00                            |

\* Source: Chiroma T. M. et al. (2014).



**Figure 1.** Chromatogram obtained for Sample A.

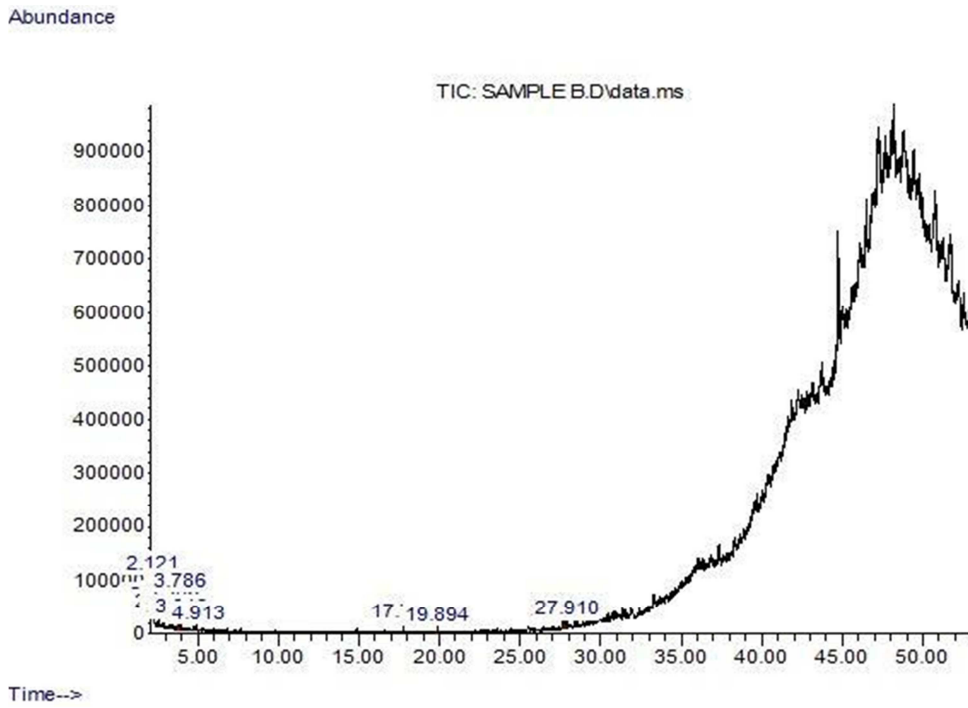


Figure 2. Chromatogram obtained for Sample B.

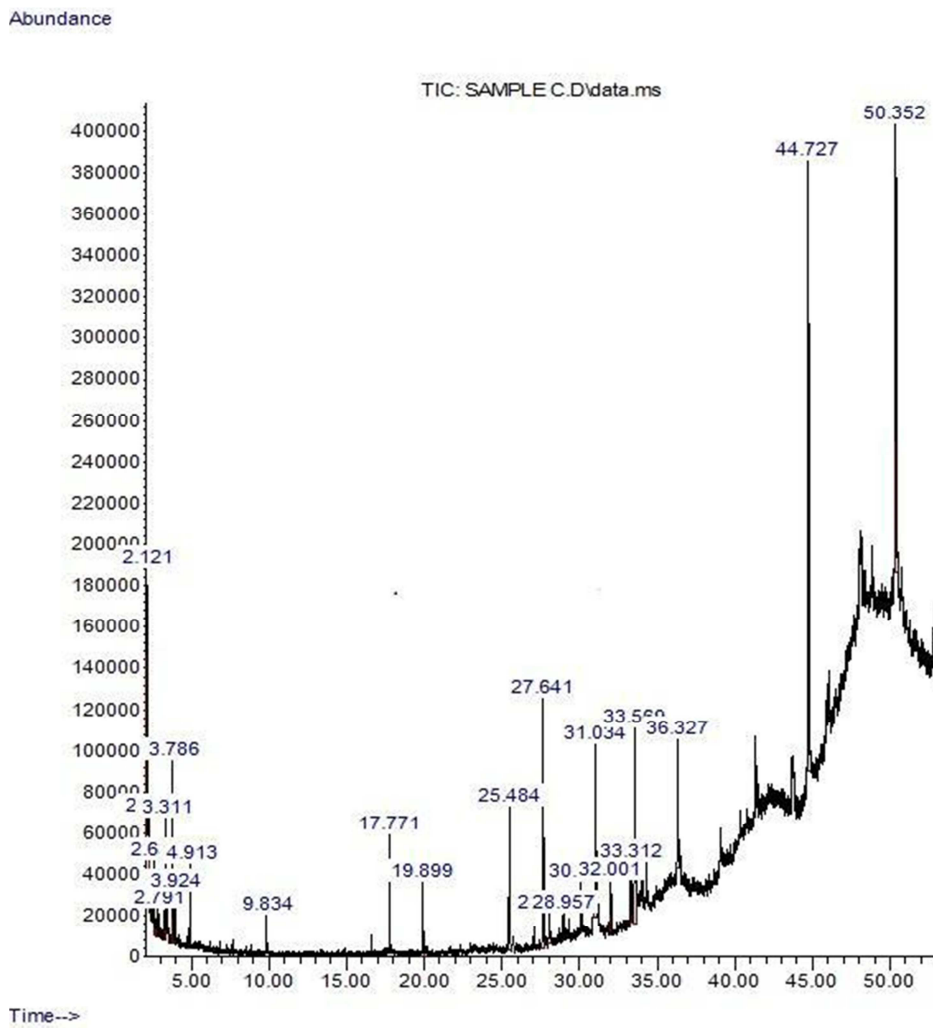


Figure 3. Chromatogram obtained for Sample C.

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