

## Investigation of some Persistent Organic Pollutants in Soil around selected Auto-Mechanic Workshops in Osogbo

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**Abstract:** Public health is at risk due to pollution from activity in car workshops as the quality of the soil near auto businesses has received less attention. This study assessed soil quality in auto shops in Osogbo, Osun State, South-West Nigeria. Two car workshops were chosen and soil samples were collected from two different points each using a random survey method (i.e., picked two sites randomly). The soil samples were collected at irregular positions within the vicinity of the two auto repair shops at 0–20 cm and 20–40 cm depth. The samples were taken for examination of polychlorinated biphenyls (PCBs) and (Polycyclic aromatic hydrocarbons) PAHs. The samples were analysed in the lab according to regular technique, and 16 US EPA priority PAHs and PCBs were then examined using a gas chromatography-mass spectrometer (GC-MS). The potential toxicities were evaluated and values obtained were compared with United States permissible limits for soil quality. The total PAH values in the soil were between 0.17  $\mu\text{g}/\text{m}^3$  to 4.97  $\mu\text{g}/\text{m}^3$ , with the soil samples near the truck maintenance shops having the greatest PAH concentrations between 0 - 20 cm below the surface. The most prevalent PAH species in soil samples was Fluoranthene, followed by Fluorene and Indeno [1,2,3-cd] pyrene. Also, PCBs were found in the location with 1,1'-Biphenyl, 2,2',3,4,4',5'-hexachloro- (PCB 138) having the highest concentration value followed by 1,1'-Biphenyl, 3,3',4,4'-tetrachloro- (PCB 77). The findings of this study showed that both of these pollutants investigated are very prevalent in these areas. There is a grave environmental concern because the discovered levels of PCBs and PAHs exceed the permissible limits set by the USEPA standards.

**Keywords:** PAH, PCB, Soil, Auto workshop, Pollution

### 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) in various compartments, soil in particular, have drawn a lot of interest recently due to their acute toxicity and cancer-causing abilities [1,2]. On Earth, atmospheric PAHs are continuously deposited by dry or wet deposition processes [3].

Some PAHs are emitted from close sources, such as vehicle exhaust from neighbouring roads [4].

Other PAHs come from farther away and have travelled a great distance through the air [5]. The ability of PAHs to penetrate the soil is influenced by both the PAHs and the soil properties [6]. As a result, PAHs sorption is one of the mechanisms that control PAHs mobility in soil [6].

The 209 congeners known as polychlorinated biphenyls (PCBs) are a combination of biphenyls containing one or more chlorine atoms [7]. Due to their slow rate of degradation, polychlorinated biphenyls (PCBs)

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are a family of semi-volatile organic compounds (SVOCs) that are dangerous and persistent in the environment [8]. PCBs are persistent in the environment because they can travel over great distances in the background and securely adhere to soil and sediment [9]. Numerous harmful health effects, including immune system impairment, neurological system changes, endocrine disruption, gastrointestinal bleeding, and liver damage, have been linked to PCBs exposure if found in substantial amounts above the permissible level [10]. Since the 1970s, the production of these substances has been increasingly banned or restricted due to their persistence and toxicity to the surrounding [11].

The service industry sector is not complete without auto shops. Unfortunately, the disposal of wasted motor oil and wash water into the earth is the present workshops' worst environmental impact. Waste oil is a complex mixture of compounds, including petroleum hydrocarbons, chlorinated biphenyls, chlorodibenzofurans, additives, by-products of decomposition, and heavy metals that are released as engine parts deteriorate. The soil loses its beneficial qualities, such as fertility, water-holding capacity, permeability, and binding capacity, when it is contaminated by oil. Nigeria, like many other nations, has substantial petroleum hydrocarbon contamination. One of Nigeria's environmental issues is pollution from the disposal of spent motor oil, which is more pervasive than pollution from crude oil [12]. An estimated 20 million gallons of used engine oil are produced annually in mechanic shops [12]. Unfortunately, used oil management practices are not standardized in Nigerian car shops. As a result of this, oils are carelessly released into the environment. By reason of the presence of heavy metals, aromatic hydrocarbons, and other

contaminants, oil spilt into the atmosphere has detrimental effects on plants, animals, and people's health [13]. Used batteries, oxidation products from machinery wear, sediments, water, and organic and inorganic chemicals used in metals and oil additives are just a few of the contaminants found in used oil from automobiles [14].

As stated by World Health Organization (WHO), environmental factors are thought to be responsible for 23% of fatalities in developing nations [15]. Exposure to hazardous and persistent materials may have negative effects on more than 200 million individuals worldwide [16]. Pesticides, heavy metals, PCBs and PAHs have all been identified as dangerous and persistent xenobiotic pollutants that accumulate in environmental media and constitute a major health concern [17].

PAHs and PCB are organic pollutants that seriously affect human health. Sufficient information is not presently available in the open literature on the soil levels of these pollutants in automobile mechanic workshops in Nigeria, hence this study. According to Nwachukwu *et al.*, [18], the country's subpar waste management of mechanic workshops is seriously endangering the environment and the general people. Engine oil, diesel, gasoline, and kerosene are examples of petroleum products that mechanics frequently use in their shops. They demonstrated that the inappropriate disposal of these goods, whether in small or big amounts, and spills caused by them, cause environmental damage.

In recent research carried out on auto-mechanic workshops effects groundwater and soil in the Ibadan metropolis, it was reported that auto-mechanic workshops daily activities negatively impact soil and water [19]. It was

thus advised that mechanic villages be located away from residential areas, that local plants be used to phyto-remediate polluted soil, and that automobile workers receive ongoing education and training that emphasizes the negative environmental effects of their subpar waste management practices.

As long as there are vehicles on our roadways, there will always be a demand for auto mechanics. The increasing influx and importation of attractively used vehicles into Nigeria have led to the emergence of numerous mechanic shops around the nation. People who work in auto repair or mechanic currently use open unoccupied plots and farmlands as workshops. Large-scale pollution has been continuously introduced into the environment, which is closely related to the growing industrialization and urbanization processes. One such activity is auto maintenance. Working with products that can contaminate the environment, such as paints, diesel, greases, oils, gasoline, diesel, battery electrolyte and other substances, is a common occurrence in auto mechanic workshops [20]. Research have demonstrated that incorrect waste treatment or disposal can cause wastes produced as by-products of vehicle repair activities to pollute the environment [21, 22]. This study's primary goal is to examine and quantify the amount of PCBs and PAHs in soil taken from several auto-mechanic workshops using standard soil quality regulations.

## II Materials and Method

### A. Area of Study

The concentration and levels of PCBs and PAHs in the soil around auto-mechanic workshops located within Osogbo, Osun State, Nigeria were evaluated. The locations were chosen due to the over congestion of

auto mechanic activities in the area. The research locations include a mechanic workshop for cars with coordinates 07°45'39", 04°34'60" " and a mechanic workshop for trucks and heavy-duty machines with coordinates 07°45'38", 04°34'54".

### B. Collection of Soil Sample

Soil samples were collected from two separate points using a random survey method (i.e., picked two sites randomly). The samples were collected at irregular positions but a known distance from each other. In the vicinity of the two auto repair shops in Osogbo city, a total of 8 samples were taken, 4 of which were taken for examination of each PCBs and PAHs, respectively. For each sampling site, samples of 1 kilogram each were taken at depths of 0–20 cm and 20–40 cm. The layer of the topsoil uppermost detritus was removed and the soil sample was then put into a Ziploc bag and taken to the lab for examination.

### C. Preparation of Samples

In a glass centrifuge tube with a 15 mL capacity, the samples were extracted. Samples were spiked with 20  $\mu\text{L}$  ( $10 \mu\text{g mL}^{-1}$ ) of an internal standard that was isotopically labelled, and they were left to stand for at least 60 minutes at room temperature to reach equilibrium. After that, samples were extracted in a Soxhlet extractor using a 10 mL solution of acetone/hexane (1/1), followed by 5-minute centrifugation at 4500 x g. By using a mild nitrogen flow, the extracts were mixed, reduced to 0.5 mL, exchanged for hexane, and cleaned up using offline acidified silica gel solid phase extraction. At a flow rate of roughly 3 mL min<sup>-1</sup>, 10 mL MeOH and 10 mL hexane are used to condition the acidified silica. The SPE cartridge received the extracts after the transfer. The extracts were transferred to the SPE cartridge and eluted

with a 12 mL mixture of hexane/dichloromethane (1/1). Eluent solutions were concentrated under a gentle stream of nitrogen to nearly dry and then refilled with 1 mL of hexane. These samples were subjected to analysis by GC-MS.

#### D. Determination of PAHs in Samples

The extract was analysed using a Varian GC-MS 4000/3800 mass spectrometer (Agilent Technologies Standard solutions containing all 16 target compounds at concentrations ranging from 0.5 to 50 pg/ $\mu$ l were used to calibrate the GC-MS (PAHs Standard). Prior to the analysis, the extract was separated using a Varian GC-MS 4000/3800 gas chromatograph (Agilent Technologies, Palo Alto, CA) using an HP-1MS (Cross-linked PH ME siloxane) 19091S-933 of 1  $\mu$ m column 60 m x 0.32 mm and a stationary phase thickness.

#### E. Determination of PCBs in Samples

Five PCBs congener standard solutions, hexane and acetone were used to prepare a standard solution for calibration including a full suite of 209 PCB congeners. The concentration of PCBs in the samples were measured using a gas chromatograph connected to a mass selective detector (Agilent Model 7890A / Agilent 5972). An HP-5 fused silica capillary column (5% phenyl-95% dimethyl polysiloxane) with a 30 m length x 0.25 mm i.d., x 0.25  $\mu$ m film thickness was utilized for the separations. The column was initially set at 120  $^{\circ}$ C (withholding time: one minute), and then increased to 190  $^{\circ}$ C at a rate of 20  $^{\circ}$ C  $\text{min}^{-1}$ , then to 230  $^{\circ}$ C at a rate of 5  $^{\circ}$ C  $\text{min}^{-1}$ , and ultimately to 300  $^{\circ}$ C at a rate of 25  $^{\circ}$ C  $\text{min}^{-1}$  (withholding time: ten min). Temperatures were established for the injector and transfer line at 280 and 300  $^{\circ}$ C, respectively.

#### F. Evaluation of Toxicity

The health risk from breathing contact was evaluated by using the methods provided by USEPA [23] and [24]. The potential toxicity of PAHs in the soil is assessed using the most carcinogenic PAH, Benzo[a]pyrene. Standard TEF were obtained from USEPA (2011) and their values are provided in Table 1 below. The potential toxicity is calculated using the formula herein represented as Equation 1:

$$\sum TEQ = TEF_i \times \sum C_i \quad \text{Equation (1)}$$

where;  $C_i$  = mean concentration level of the individual PAH compound

$TEQ$  = toxic equivalent quotient

$TEF_i$  = toxic equivalent factor relative to Benzo[a]pyrene.

$TEFs$  used were obtained from US EPA [23] and [24].

### III. Results and Discussion

#### A. Concentration of PAHs and PCBs in Soil

Figures 1 and 2 below show the mean concentrations of PAH and PCB, respectively, in soil samples taken from the two sampling sites. The locations sampled showed a sum of sixteen PAHs, they were found in the soil at varied quantities, proving that the PAHs concentration in the soil sample did not follow a predictable distribution pattern. The total EPA PAH values in the soil between 0.17  $\mu\text{g}/\text{m}^3$  and 4.97  $\mu\text{g}/\text{m}^3$ , with the soil samples near the truck maintenance shops having the greatest PAH concentrations between 0 - 20 cm below the surface. The most prevalent PAH species in soil samples was Fluoranthene, followed by Fluorene and Indeno [1,2,3-cd] pyrene. The truck repair shops samples with a depth of 0–20 cm had high levels of Acenaphthylene. Chrysene and Dibenzothiophene have low quantities at the car sampling location. Only one occurrence of Dibenzothiophene was found at truck

sampling sites at a depth of 20–40 cm, and no more occurrences were found. The depth of 0–20 cm contains the largest amount of Chrysene ( $4.97 \mu\text{g}/\text{m}^3$ ).

**Table 3.2: TEQ for sand samples ( $\mu\text{g}/\text{m}^3$ )**

S/N	PAHs Detected in sand	TEF	TEQ			
			Car		Truck	
			0-20cm	20-40cm	0-20cm	20-40cm
1	Naphthalene	0.001	0.00086	0.00084	0.00083	0.00084
2	Acenaphthylene	0.001	0.00077	0.00038	0.00191	0.0004
3	Dibenzothiophene	0.1	0.02	0.022	-	0.023
4	Acenaphthene	0.01	0.0129	0.0078	0.0138	0.0187
5	Fluorene	0.001	0.00337	0.0034	0.0038	0.00409
6	Phenanthrene	0.001	0.00204	0.00207	0.00205	0.00266
7	Pyrene	0.001	0.00165	0.00139	0.0025	0.00227
8	Fluoranthene	0.08	0.324	0.3232	0.3184	0.3952
9	Anthracene	0.01	0.0133	0.0137	0.0118	0.0141
10	Chrysene	0.01	0.0085	0.0086	0.0345	0.0108
11	Benzo[a]pyrene	1	-	-	0.2	0.2
12	Benzo[a]anthracene	1	2.19	2.17	2.03	2.02
13	Indeno[1,2,3-cd]pyrene	0.1	0.361	0.358	0.39	0.395
14	Benzo[b] Fluoranthene	0.1	0.206	0.28	0.168	0.118
15	Dibenzo[a,h]anthracene	1	1.94	3.4	2.05	2.24
16	Benzo[ghi]perylene	0.01	-	0.0023	0.0017	0.0021
$\Sigma\text{TEQ}$			5.08439	6.59368	5.22929	5.44716

In the car sampling site, Benzo[a]pyrene was identified at all, it was found once in the truck sampling sites. According to the discussion above, the soil at the mechanic workshop had the highest content of 16 EPA PAHs with a depth of 0–20 cm ( $31.11 \mu\text{g}/\text{m}^3$ ), which contributed to the bulk. The system of classification for soil pollution used by the European Commission states that 16 EPA PAHs < 0.20 mg/kg, between 0.20 mg to 0.60 mg/kg, between 0.60 mg to 1.0 mg/kg and > 1.0 mg/kg, respectively, indicate no contamination, weak

contamination, moderate contamination and heavy contamination, respectively [25]. It can be concluded from this classification that the soil in the research region is moderate to heavily polluted.

A total of twenty-six PCBs were found in the location with PCB 138 (1,1'-Biphenyl, 2,2',3,4,4',5'-hexachloro-) having the highest concentration value followed by PCB 77 (1,1'-Biphenyl, 3,3',4,4'-tetrachloro-). These PCBs have been reported to be one of the causes of nervous and cancer problems, and thus possess deleterious health effects.

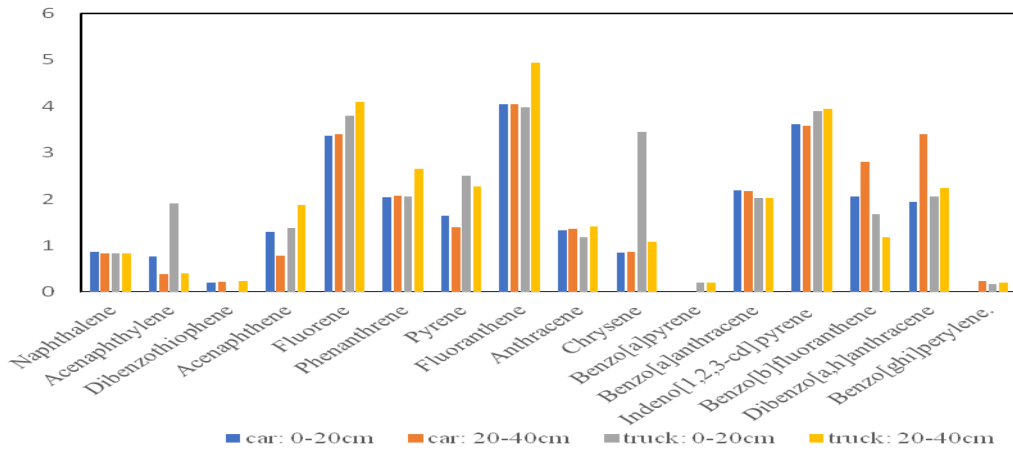


Figure 1: Characterized polycyclic aromatic hydrocarbon compounds in soil

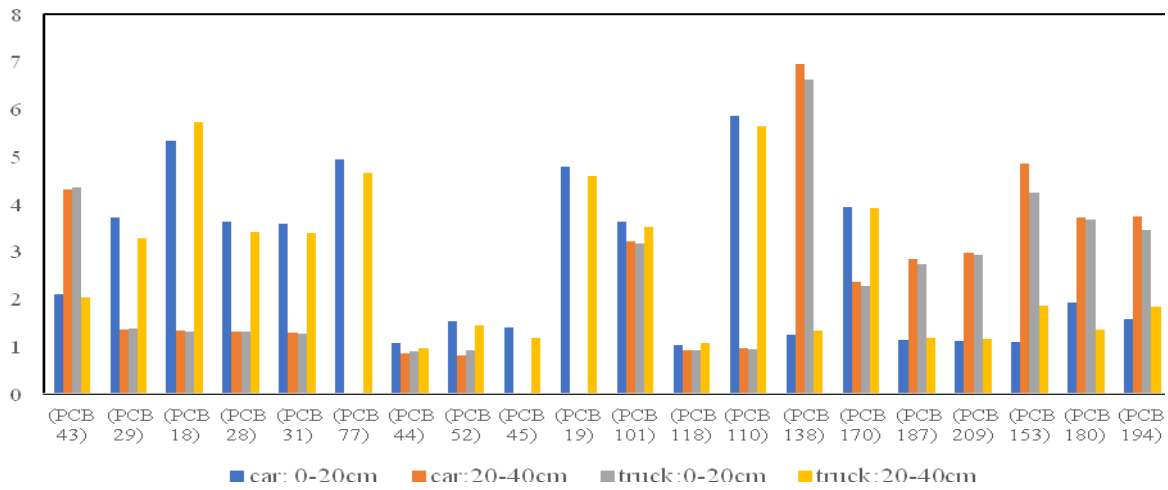
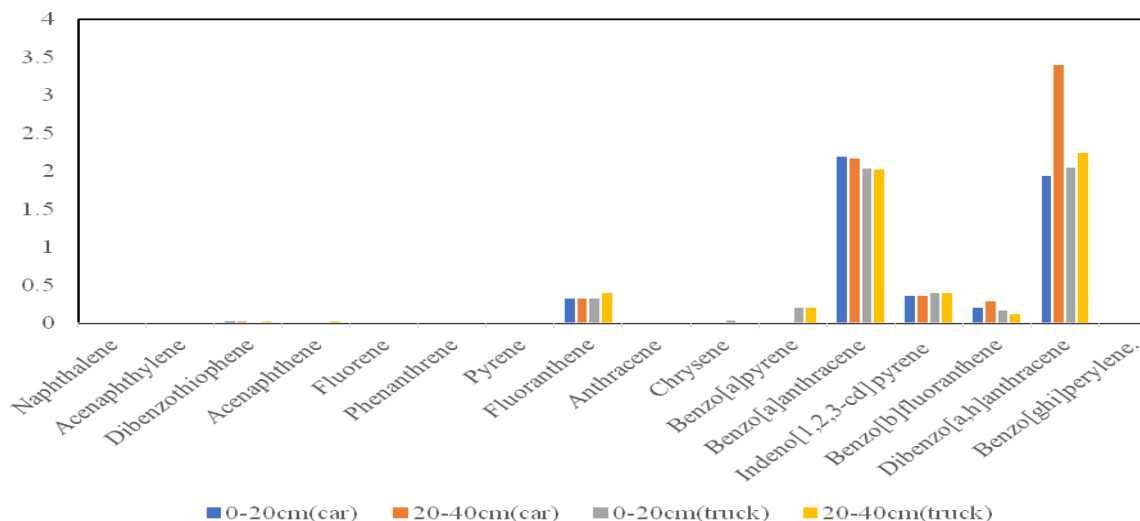


Figure 2: Characterized polycyclic biphenyls compounds in soil



**Figure 3: TEQ values for PAHs in soil**

### B. Toxicity Equivalence of PAHs

The toxicity equivalent factor and the results for each PAH are displayed in the chart below. Dibenzo[a,h]anthracene, which has a weight of  $3.4 \mu\text{g}/\text{m}^3$  and predominates in the soil of the maintenance shop for trucks and caterpillars, was found to have the highest TEQ values among all samples. Benzo[a]anthracene, Indeno[1,2,3-cd]pyrene, Benzo[b]fluoranthene

and Benzo[a]pyrene with TEQ values of 2.19, 0.36, 0.28 and  $0.2 \mu\text{g}/\text{m}^3$ , respectively, were additional substantial contributions. The component that predominated in the soil sample was dibenzo[a,h]anthracene ( $3.4 \mu\text{g}/\text{m}^3$ ). All but one of the sites contained Benzo[a]pyrene, with the second truck having the highest concentration

### IV. Conclusion

The results of this study, which examined the concentrations, sources, and effects of PCBs and PAHs on the soil quality of two mechanic shops in Osogbo, revealed that these pollutants are both considerably present in large numbers in these locations. The majority of the pollution was discovered in the soil of the mechanic shops, which may have occurred as a result of routine vehicle maintenance, repairs, and other activities performed there. There is a severe ecological concern because the discovered amounts of PCBs and PAHs are higher than the allowed limits established by European states.

The presence of pollutants in quantities that are higher than the permitted limit means that those who live nearby are at increased risk of developing cancer. The mechanic shop's vehicle repair and other services may cause the pollutants in these study locations to build up, which could eventually have an impact on the groundwater and nearby surface water resources. In order to prevent any potential health concerns brought on by increased levels of PAHs and PCBs resulting from auto professionals performing vehicle maintenance or servicing, it is imperative to regularly monitor activities in mechanic workshops. Strict legislation should also be implemented to help regulate the acts of car mechanics in

vehicle repair shops in order to help prevent PAH and PCB contamination of the environment. Further study should be conducted as well as proper monitoring of the accumulation of pollutants in the groundwater at different distances to

investigate the degree to which the soil is contaminated in these workshops. It is also recommended that auto mechanic workshops should be located far away from residential buildings

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