



Determination of levels of polycyclic aromatic hydrocarbons in soil contaminated with spent motor Engine oil in Abakaliki Auto-Mechanic Village

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ABSTRACT: Soil samples contaminated with spent motor engine oil collected from Abakaliki auto-mechanic site were analyzed to determine the concentration of polycyclic aromatic hydrocarbon (PAH) components which are often targets in environmental check. Identification and quantification of the PAH components was accomplished using a gas chromatographic system (6890 series and 6890 plus) equipped with a quadrupole Mass Spectrometer (Agilent 5975 MSD) after ultrasonic extraction of the sample and clean up of the extract. The results showed that out of the sixteen USEPA target PAHs (EPA-16) assayed, only six were detected in varying concentrations in mg/kg. These include Phenanthrene with concentration range of 0.0172 ± 0.01 to 0.0193 ± 0.02 , fluorene (0.0189 ± 0.01), benzo[a]anthracene (0.0162 ± 0.05), chrysene (0.0209 ± 0.02), benzo[b]fluoranthrene (0.0453 ± 0.02) and benzo[k]fluoranthrene (0.0389 ± 0.1). The concentration of total PAH components detected in the samples ranged from 0.0184 ± 0.02 to 0.1385 ± 0.2 mg/kg. Implications of PAHs on health were discussed. ©JASEM

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In Nigeria, as in many other countries, petroleum hydrocarbon contamination is widespread. Pollution arising from the disposal of used engine oil is one of the environmental problems in Nigeria and is more widespread than crude oil pollution (Odjegba and Sadiq, 2002). The prevalent mode of indiscriminate disposal of these spent engine oils in the environment calls for urgent attention. Contamination results from mishandling, deliberate disposal, spilling and leakage of petroleum products, such as gasoline, lubricating oils, diesel fuel, heating oils, used or spent engine oils. A survey of Abakaliki capital city of Ebonyi State, Nigeria indicates that apart from the centralized Abakaliki auto-mechanic workshops cluster (popularly called mechanic village or site), there are several other automobile workshops scattered all over the town from which used engine oils, lubricating oils and other solvents containing petroleum hydrocarbons are indiscriminately dumped or spilled on every available space by artisans in the business of auto-repairs. The local utilization of engine oil in Abakaliki has increased in the recent time owing to new status of Abakaliki as a capital city following the creation of Ebonyi State in the last 17 years. This is due to the upsurge in the number of vehicles and other machines that makes use of these lubricants. These unguided practices have worsened the rate at which used engine oils spread and contaminate the soils and water around the town. Studies in auto-repair workshop sites have been carried out by many researchers (Ipeaiyeda and Dawodu, 2008). But most of them focused on the study of the implication of heavy metal contamination in soil by these used engine oils without recourse to the effects of other petroleum hydrocarbon pollutants such as the persistent and ubiquitous polycyclic aromatic hydrocarbons (PAH) present in used engine oils. These used oils and solvents form part of the most

hazardous wastes commonly generated in auto-repair shops around cities in Nigeria (Ipeaiyeda and Dawodu, 2008 and Iwegbue, 2007). Waste oil is a mixture of different chemicals including petroleum hydrocarbons, chlorinated biphenyls, chlorodibenzofurans, additives, decomposition products and heavy metals that come from engine parts as they wear away (Wang *et al.*, 2000; ATSDR, 1997). Used engine oil, also called spent lubricant or waste engine oil, is usually obtained after servicing and subsequently draining from automobile and generator engines (Sharifi *et al.*, 2007). The exact composition of used oils depends on the origin, extent of use and degradation products that formed in the oil over time or during use. Ekundayo *et al.*, (1989) have shown that noticeable changes in properties occur in soils polluted with petroleum hydrocarbons arising from used engine oils. Oil pollution of soil leads to build up of metals in soil and the eventual translocation in plant tissues (Vwioko *et al.*, 2006). Used engine oil easily migrates into the environment and eventually seeps into water bodies (Olugboji and Ogunwole, 2008).

PAHs belong to a group of over 100 hazardous substances of organic pollutants consisting of two or more fused-benzene aromatic rings. Formation of PAH is due to incomplete combustion of organic matter through the condensation of ethylenic radicals in the gas phase to form the larger polycyclic compounds (Lane, 1989). Those containing up to four benzene rings are known as light PAHs (l-PAHs) and those containing more than four benzene rings are known as heavy PAHs (h-PAHs). The h-PAHs are more stable and toxic than the l-PAHs (ATSDR, 1995). According to Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) list of hazardous substances, PAHs

ranked 7th in 2005 in the biennial ranking of chemicals deemed to pose the greatest possible risk to human health (Christopher, 2008). PAHs have low solubility in water and are highly lipophilic. In water or when adsorbed on particulate matter, PAHs can undergo photodecomposition in the presence of ultraviolet light from solar radiation. In the atmosphere, PAHs can react with ozone, nitrogen oxides and sulphur dioxide, to give diones, nitro- and dinitro-PAHs, and sulphonic acids, respectively. Biologically, PAHs can be degraded by some microorganisms in the soil (WHO, 1987 and ATSDR, 1994). Some have been demonstrated to be mutagenic and carcinogenic in humans (Phillip, 1999). Those PAHs that have not been found to be carcinogenic may, however, synergistically increase the carcinogenicity of other PAHs. The main focus of this study was to find the background levels of PAHs within the ever increasing human effected build-up

area of Abakaliki Auto-mechanic village which has become densely populated with residential homes.

MATERIALS AND METHOD

The Study Area: The study area was Abakaliki auto-mechanic village located along the old Abakaliki-Ogoja Expressway a few meters to the popular Abakaliki Rice Mill cluster. The Abakaliki, auto-mechanic village lies within Lat. 6.20N and Long. 8.10E (Fig. 1). It is an area mapped out by the government of Ebonyi State for artisans in automobile business which involves constant changing of used motor engine oils. The Abakaliki auto-mechanic village is one of the busiest areas in the town considering the volume of other business activities that sprang up following the new state creation.

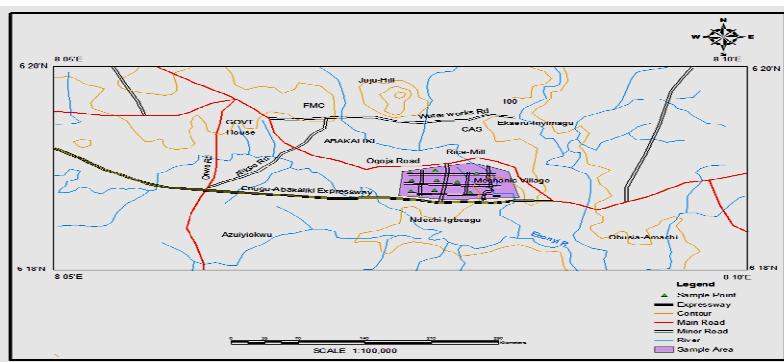


Fig. 1: Map of Abakaliki Showing the Study Area and Sample points

Sampling, Collection and Treatment: The sample area was divided into three sub-areas. In each of the sub-areas, three workshop sites were selected randomly for sample collection. Three soil samples were collected from each sub-area and homogenized into a composite sample. The samples were collected with an improvised soil augur (nitric acid sterilized PVC pipes) in June, 2012 between the hours of 8-10am. A total of nine batch soil samples made into three different composite samples were collected at depth of 0-15 cm, after the removal of the exposed surface according to MCPA method (2008). A thin layer of the composite samples were screened on a filter paper to remove fragments of plants debris and stone. The screened samples were thereafter air-dried in the dark. The dry soil samples were then ground into powder in a ceramic mortar and demagnetized with a magnetic rod and kept in sealed vials labelled EZW, Q265W and NCPW (Table 1). They were preserved in a refrigerator at 4°C according to the US-EPA recommended sampling protocols (Method 8100) prior and GC-MS analysis.

Sample Extraction and GC-MS Analysis: Extraction of hydrocarbons from the samples was done with a sonicator (Ultrasonic bath-Elmsonic S40H) in accordance with US SW-846 Method 3550. A 10.00g of each of the composite samples was extracted with a 50:50 mixture of acetone and methylene chloride spiked with 1 ml of PAH internal standard and shaken thoroughly for proper mixing before placing in an ultrasonic bath. The EPA-16 PAHs determination was conducted at Dukoria Laboratories Limited, Warri, Delta State, Nigeria using Gas Chromatographic System (6890 series and 6890 plus) equipped with a dual detector (FID-ECD), dual column and TriPlus AS auto-sampler with helium carrier gas and a quadrupole Mass Spectrometer (Agilent 5975 MSD) based on USEPA method 8100 (EPA, 1984). A 2.00µl of extracts were injected into the GC port set at column conditions: HP-5 crosslinked PH-ME siloxane, Length of 30 m, I.D: 0.25 mm, thickness of 1 µm with helium carrier gas set in the splitless, constant flow mode with 1.2 ml/min flow rate. Other GC and MS operating set-up were done according to the instrument's method development as specified in the operating instruction

manual. Identification and quantification of individual PAHs was based on internal calibration standard containing known concentrations of the 16 PAHs (EPA-16). The specificity of the 16 PAHs sought for in the samples was confirmed by the presence of transition ions (quantifier and qualifier) as shown by their retention times which corresponded to those of their respective standards. The measured peak area ratios of precursor to quantifier ion were in close agreement with those of the standards. Results

obtained were presented as mg/kg concentration per analyte.

RESULTS AND DISCUSSION:

The concentrations of the 16 EPA Target PAH components (mg/kg) in the soil samples collected from Abakaliki auto-mechanic site are presented in Table 1 and Fig. 2. The GC-MS fingerprints confirming the presence of these analytes in the samples are shown in Figs. 3-5.

Table 1: Concentrations of 16 EPA Target PAH Components assayed in the Soil Samples

PAH Component (mg/kg)	EZW	Q265W	NCPW
Naphthalene	nd	nd	nd
Acenaphthalene	nd	nd	nd
Acenaphthene	nd	nd	nd
Fluorene	nd	nd	0.0189±0.4
Phenanthrene	0.0184±0.22	0.0172±0.2	0.0193±0.25
Anthracene	nd	nd	nd
Fluoranthene	nd	nd	nd
Pyrene	nd	nd	nd
Benzo[a]anthracene	nd	0.0162±0.3	nd
Chrysene	nd	0.0209±0.4	nd
Benzo[b]fluoranthrene	nd	0.0453±1.5	nd
Benzo[k]fluoranthrene	nd	0.0389±1.4	nd
Benzo[a]pyrene	nd	nd	nd
Indeno[1,2,3-cd]perylene	nd	nd	nd
Dibenzo[a,h]anthracene	nd	nd	nd
Benzo[g,h,i]perylene	nd	nd	nd
Total	0.0184±0.02	0.1385±0.2	0.0381±0.03

Values represent mean±standard deviation of three replicates; nd = not detected

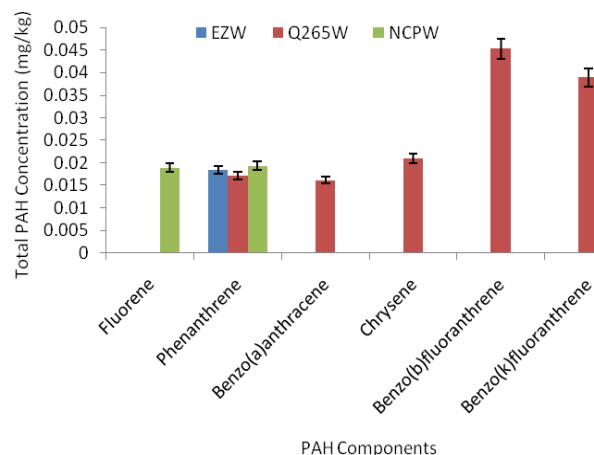


Fig. 2: Total Concentration of PAH detected in each of the Soil Samples

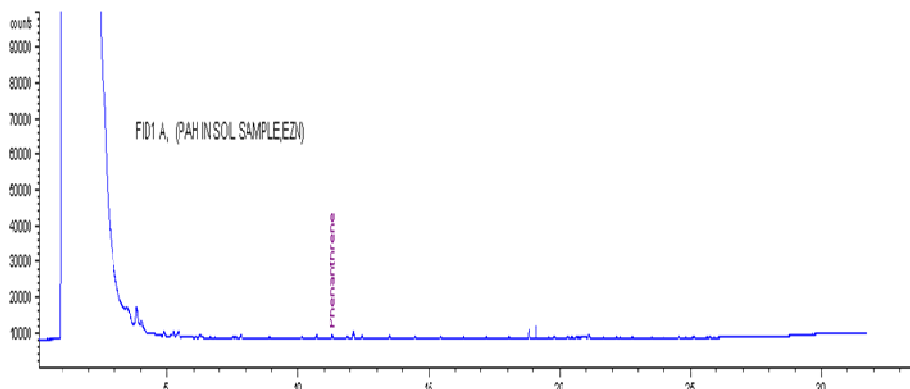


Fig. 3: PAH in EZW Sample

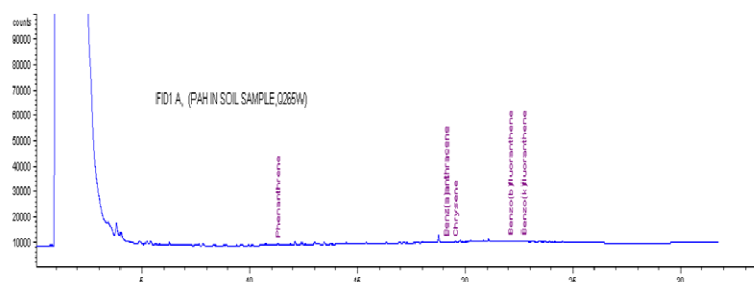


Fig. 4: PAHs in Q265W Sample

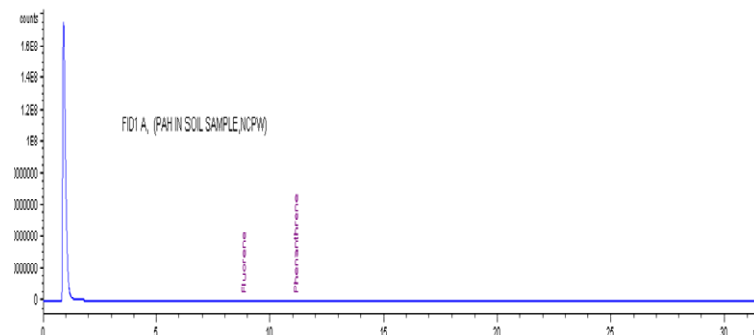


Fig. 5: PAHs in NCPW Sample

The results of the concentration (mg/kg) of the 16 EPA PAH compounds investigated in the contaminated soil site as shown in Table 1 and Fig. 2 respectively, indicated the presence phenanthrene in the studied composite samples. Concentration of phenanthrene ranged from 0.0172 ± 0.01 to 0.0193 ± 0.02 in all the samples. Sample Q265W showed the highest number of PAHs namely, phenanthrene (0.0172 ± 0.01), benzo[a]anthracene, (0.0162 ± 0.05), chrysene (0.0209 ± 0.02), benzo[b]fluoranthrene (0.0453 ± 0.02) and benzo[k]fluoranthrene (0.0389 ± 0.1) at varying concentrations that are significantly different. In sample NCPW, only fluorene and phenanthrene were detected. The total PAH concentration in the samples differed significantly with sample Q265W having the highest PAH concentration load of 0.1385 ± 0.2 and sample EZW had least (0.0184 ± 0.02). The very low molecular weight PAHs such as naphthalene,

acenaphthalene and acenaphthene were not detected probably due to the high volatilization or dissolution which may have occurred during the process of extraction. It may also be due to the length of time of exposure of the soil samples prior to this study.

The results also showed that phenanthrene and benzo[b]fluoranthene PAHs constituted the largest group of compounds with high concentrations in a typical soil sample contaminated with used engine oils, with the low molecular weight phenanthrene being more dominant with relatively lower concentrations compared to benzo[b]fluoranthene. It is evident from the results that the soils of Abakaliki auto-mechanic site were contaminated with PAHs at varying concentrations. However the total PAH concentrations were very low when compared with the maximum background limits of 15mg/kg and 50mg/kg in polluted soils set by Dutch and Polish

Environment Ministries respectively, (Polish Environment Ministry, 2002). This low values recorded in this study should not be taken for granted since there is no threshold concentration below which carcinogenic effects of PAH does not occur. The six PAH components detected fall within the category of PAHs with the highest health risk especially at prolonged exposure (ATSDR, 1999a). Four out of the six PAHs namely benzo(a)anthracene, chrysene, benzo(b)fluoranthrene and benzo(k)fluoranthrene are implicated as carcinogens according to the US-EPA (California Environmental Protection Agency, 1994). Consequently, it is feared that the population of people living in and around the Abakaliki auto-mechanic village may be predisposed to high risk of cancer due to long-term exposure to PAH compounds through contaminated soils and water.

The health effects of PAHs have been reviewed extensively. These effects depend mainly on the extent of exposure, dose, innate toxicity and exposure routes. Other pre-disposing factors include pre-existing health status and age. There is risk of harm in both short and long term exposure especially among the artisans. PAHs are ubiquitous in the urban and rural environment. As a result, it is very common to detect levels of PAHs in soils even at low levels and its toxicity consideration is of utmost importance. PAHs pose a major threat in terms of its carcinogenic effects. Some studies have shown that heavy PAHs can induce dioxin-like activity and weakened estrogenic responses (Villeneuve *et al.*, 2002).

The chemistry and toxicity of PAHs are best understood using benzo[a]pyrene which has been extensively studied with a well established chemistry of its carcinogenic effects (Lee and Shim, 2007). Its metabolites were said to be mutagenic and highly carcinogenic, and is listed as a Group 1 carcinogen by the International Agency for Research on Cancer (IARC). The compound is one of the benzopyrenes, formed by a benzene ring fused to pyrene, and is the result of incomplete combustion at temperatures between 300°C and 600°C (Aygün and Kabadayi, 2005). Benzo[a]pyrene toxicity results from its bioactivation to the ultimate toxic compound, benzo[a]pyrene-7, 8-dihydrodiol-9,10-epoxide (Shou *et al.*, 1996). Benzo[a]pyrene-7,8-dihydrodiol-9,10-epoxide is the carcinogenic product of three enzymatic reactions (Hao Jiang *et al.*, 2007). Properly speaking, benzo[a]pyrene is a pro-carcinogen, meaning that the mechanism of carcinogenesis of benzo[a]pyrene depends on enzymatic metabolism of benzo[a]pyrene to the ultimate mutagen, which is benzo[a]pyrene diol epoxide. X-ray crystallographic and nuclear magnetic resonance structure studies show that this binding distorts the DNA (Shou *et al.*, 1996) inducing mutations by perturbing the double-helical DNA structure. This disrupts the normal

process of copying DNA and induces mutations. This explains the occurrence of cancer after exposure (Eaton and Gallagher, 1994). Research also indicated that benzo[a]pyrene diol epoxide specifically targets and destroys the protective gene thereby leading to cancer (Pfeifer *et al.*, 2002; Daniel, 2007).

Conclusion: It is evident from this study that the Abakaliki auto-mechanic site is gradually being contaminated with PAHs arising from indiscriminate disposal of spent crankcase engine oils. As the city is expanding with more business outlay emerging, recycling and re-use advocacy is being recommended to track the spread of waste oils in the environment. The risk associated with the PAHs components of the spent engine oils are grave and needed to be tracked and regularly monitored not only in soils but also in water, air, vegetables and other plants in the area.

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