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Assessment of the Polycyclic Aromatic Hydrocarbons (PAHs) and Heavy Metal Contents of Abattoir Soils

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ABSTRACT

The use of organic fuel sources in open fire dressing of animals results in the production of Polycyclic aromatic hydrocarbons (PAHs) being released into the environment and which constitute public health hazard. This study investigated the PAH and heavy metals content of four abattoirs soils (Igbogene, Tombia, Opolo, Swale) and a control soil (Azikoro) all located in Bayelsa State, Nigeria. Soil samples (500g) made up of three composite samples were collected with the aid of a hand soil auger at about 0-15cm depth. The soil samples were analyzed for 16 priority PAHs and heavy metals using gas chromatographic and spectrophotometric analysis respectively. Results obtained showed the absence of Acenaphthene, Acenaphtylene in all the abattoir soil samples. Benzo(a)anthracene (1.50µg/kg) and Phenanthrene (0.14µg/kg) were found in only Igbogene and Tombia soils respectively. Anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene and Chrysene recorded the highest values of 4.99, 6.9, 19.18 and 9.83µg/kg respectively in Igbogene soil. The highest values of Benzo(g,h,i)perylene (22.11µg/kg), Benzo(k)fluoranthene (113.99µg/kg), Dibenz(a,h)anthracene (25µg/kg), Fluorene (17.14µg/kg), Naphthalene (46.93µg/kg), 2-methylnaphthalene (29.95µg/kg), and Pyrene (298.9µg/kg) were recorded in Swale soils. Tombia soils recorded highest values of Fluoranthene (33.09µg/kg) and Indeno(1,2,3 cd)pyrene (38.31µg/kg). Swale recorded highest concentration of total PAHs which was followed by Tombia, Igbogene, Opolo while Azikoro (control) had the least value. For the heavy metals, Fe was highest at all locations. Highest values of Pb (21.67 mg/kg), and Fe (857.4mg/kg) were recorded in Tombia. Swale recorded highest value of 6.08mg/kg in Cd, Opolo soil samples had highest values of Cr and Ni with 8.65 and 9.66mg/kg values, respectively. The control soil had the least values of all PAHs and heavy metals analyzed which suggested that the open fire animal dressing procedures in these abattoirs are contributory to the pollution of the abattoir environment.

Keywords: Abattoir, soil, Polycyclic aromatic hydrocarbon (PAH), heavy metals, Benzo(a)pyrene, Gas Chromatography.

Introduction

Polvcvclic aromatic hydrocarbons (PAHs) are pollutants found in the environment and are well known for their mutagenic and carcinogenic effects and it can bioaccumulate in animal and human tissue. They have been classified as a class of compounds that are problematic human carcinogen, mutagen and immune suppressant (Bostrom, 2002). In 2001, PAHs were ranked ninth most threatening chemical compounds to humans (King, 2002). The carcinogenicity, teratogenicity, and genetic toxicity of PAHs have been thoroughly discussed (Kim, 2013).

PAHs can be produced from natural and anthropogenic mainly from incomplete combustion of organic materials, fossil fuel and petroleum (Aleruchi and Obire, 2020). Activities during meat processing may include smoking or drying usually from partially combusted organic fuel sources (Hamidi *et al.*, 2016) resulting in high temperatures obtained in open flames used during singeing, grilling, roasting and frying (Purcaro *et al.*, 2013; Garcias, 2016). Due to their low water solubility and high lipophilic nature, PAHs are easily and rapidly absorbed by organisms and can be accumulated in aquatic organism or adsorbed onto the surface of suspended matter, get deposited on the sea floor and be passed onto the marine food chain.

Although hundreds of PAHs exist, some of the environmentally essential PAHs referred to as priority PAHs are: acenaphthene, acenaphthylene anthracene, benz[a]anthracene, benzo[b]fluoranthene, benzo[a] pvrene. benzo[ghi]perylene, benzo[k]flouranthene, chrysene, dibenz[a,h]anthracene, flouranthene, flourene, indeno[1,2,3-cd]pyrene, naphthalene phenanthrene and pyrene. Sources of PAHs can be either petrogenic, from petroleum-related activities or pyrogenic (pyrolytic), from the incomplete combustion of gasoline, diesel fuel and engine oil. Also, the incomplete combustion of other organic fuel sources such as wood, coal, biomass of forest, grass fires, burning of agricultural wastes are all sources of PAHs. Sources of PAHs in urban atmosphere include automobiles, re-suspended soils, refineries and power plants (Omar et al., 2002; Dyke, 2003). PAHs are also widely used in commercial products, such as pharmaceuticals, intermediaries in agricultural products, photographic products, thermosetting plastics, and lubricating materials. PAHs also occur in large amounts in sedimentary rocks and petroleum (Henner et al., 1999; Lichtfouse et al., 1997). Additional contributions to ambient air levels arise from tobacco smoking (Sakai, 2002) while the use of heating sources can increase PAH concentrations in indoor air. Natural sources such as forest fires and volcanic eruptions are less important. The fate of PAHs is determined by their physicochemical properties, especially nonpolarity, liphophilicity and hydrophobicity which is responsible for their persistence in the environment. PAHs enter the environment through atmospheric deposition and direct releases of substances through petroleum spills and use, municipal wastewater treatment plants, industrial discharges, storm water runoff, landfill leachate, and surface runoff. PAHs attach readily to sediment particles, leading to high concentrations in bottom sediments of water bodies. Bioavailability of PAHs and heavy metals occurring in soil is the basic source of its accumulation in crops, herbs and soil microorganisms. The impact of soil pollution on food chain presents a challenge for many investigations.

Concentrations of PAHs in soil vary according to a variety of factors including proximity to municipal and industrial discharge points, upland activities, wind direction and distance from major urban roadways. Indiscriminate burning of organic materials, petroleum product and other industrial processes such as, markets, petrol stations, auto-mechanic villages, abattoirs as well as various runoffs from roads and railways has contributed significantly to environmental contamination by PAHs, which endangers the lives of organisms. There are several health problems associated with bioaccumulation of PAHs and heavy metals in the food chain. Long term exposure to even the simplest PAHs like Naphthalene can lead to kidney and liver damage as well as cataract. It causes redness and inflammation of skin when in contact and red blood cell damage when inhaled, Dibenzopyrene is highly carcinogenic. A major animal processing activity in the abattoirs under study include roasting and/or singeing of animal fur among others. This procedure is carried out by combustion of wood and other fuel sources. This generates smokes and its attendant complex pollutants and residues as wastes. These and other organic wastes generated from abattoirs are discharged unto the surrounding soil or river without any form of waste treatment thereby impacting the environment. This study therefore evaluates the PAHs and heavy metals concentration in soil samples from some abattoirs in Bayelsa State to determine the level of environmental deposition of these pollutants.

Materials and Methods

Sampling Location

Soil samples for this study were collected from four active abattoirs in Yenagoa Local Government Area of Bayelsa State. Control samples were collected from Azikoro (Bayelsa), a community with no record of abattoir activity. Abattoirs locations on map coordinates are indicated in Table 1.

Abattoir Location	Northing (N)	Easting (E)
Igbogene	5 [°] 2' 17.8188''	6 ⁰ 24'14.958"
Tombia	4 [°] 57' 17.8092''	$6^0 20'53.2428''$
Opolo	4 [°] 56'52.764"	6 ⁰ 20'3.984"
Swale	4 [°] 53'42.9576"	$6^0 16'39.7164''$
Azikoro (Control)	4 [°] 57' 13.77"	6 [°] 21' 19.5048"

 Table 1: Map coordinates of abattoir locations

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Sample collection

Composite soil samples (500g) constituted from three sampling points from each abattoir were collected with the aid of a hand soil auger at about 0-15cm depth. Soil samples were transported to the laboratory on ice packs and stored in the refrigerator for analyses.

Sample preparation

Polycyclic aromatic hydrocarbon components were extracted from air dried soil samples using 10ml of Dichloromethane. This extract was concentrated to 2ml by evaporating on a water bath at 400^oC. This was injected into the chromatography column packed with activated silica gel. The column was pre-eluted with 20ml of Dichloromethane. 1ml of the extracted sample was transferred into the column. The extraction bottle was rinsed with 1ml of Dichloromethane and added to the receiving end of the column as well. The stop-cork of the column was opened and the eluent was collected into a 10ml graduated cylinder. Just prior to exposure of the anhydrous sodium sulphate layer to air, Dichloromethane was added to the column in 1-2ml increments. The oven temperature was programmed from the initial 65°C (3min.) to 300°C at 25°C/m elution temperatures. Samples were automatically detected as they emerge from the column (at a constant flow rate) by the FID detector whose response was dependent upon the composition of the respective constituent fractions.

The PAHs quantification was carried out using Hewlett Packard 5890 Series II GC, U.S.A gas chromatograph. The capillary column is 30m length, 0.32mm internal diameter with Flame Ionization Detector

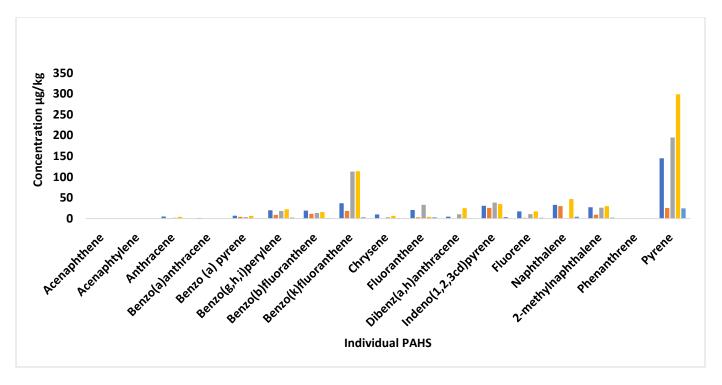
Determination of Heavy Metals

The Atomic Absorption Spectrophotometric method of APHA (1998) was used. Five grams of air dried and sieved soil was weighed into a 250 ml beaker and an empty beaker was stood in the analysis set up to represent the reagents/glass are blank. 100ml of distilled water was added, 1.0ml of concentration HNO₃ and 10ml of concentrated HCl were added respectively. The beaker was covered with ribbed watch glasses and heated at 95°C on a hot plate till the solution is concentrated to about 5ml.

The concentrates obtained (5ml) were allowed to cool at room temperature after which the solution was filtered and quantitatively transferred into a 50ml volumetric flask while diluting with distilled water to 50ml for solid matrix digest. A hallow cathode lamp for the desired metal was installed in the Atomic Absorption Spectrophotometer and the wavelength dial property set. The slit width was set for the element being measured. The instrument was turned on and allowed to warm up until energy source is stabilized. The current was readjusted as required after warm up and wavelength was optimized by adjusting the wavelength dial until optimum energy gain was obtained, the lamp was aligned accordingly. Heavy metals concentration values were read by desolvation by the chemical flame and particles absorb the light beam from the light source while the concentration of ground state atoms in the flame is directly proportional to the concentration of heavy metal of interest.

Results

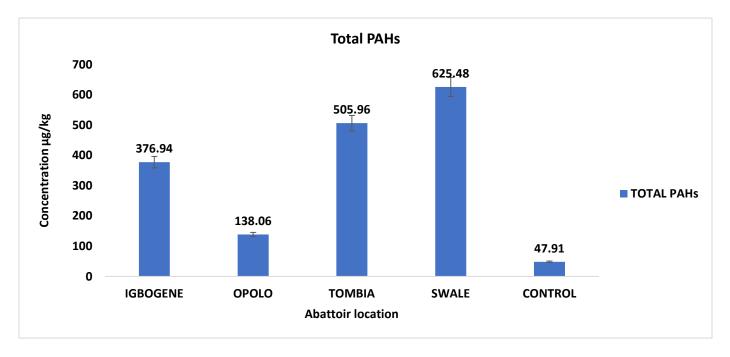
Mean concentration of individual and total PAHs in soil: Assessment of the 16 priority PAHs revealed the presence of these pollutants in varying concentrations in all the abattoir soil samples examined as indicated in Figure 1. Some PAHs components such as Acenaphthene and Acenaphtylene were not detected in all soil samples from the various abattoir locations. The result obtained showed the absence of Acenaphthene. Acenaphtylene in soil samples from all abattoir locations. Benzo(a)anthracene $(1.50 \mu g/kg)$ and Phenanthrene (0.14µg/kg) were found in only Igbogene and Tombia soils respectively. Anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene and Chrysene recorded highest values of 4.99, 6.9, 19.18 and 9.83µg/kg respectively in Igbogene soil. The highest values of Benzo(g,h,i)perylene $(22.11 \mu g/kg),$ (113.99µg/kg), Benzo(k)fluoranthene Dibenz(a,h) anthracene Fluorene $(17.14 \mu g/kg)$, $(25\mu g/kg),$ $(46.93 \mu g/kg),$ 2-methylnaphthalene Naphthalene (29.95µg/kg), Pyrene (298.9 µg/kg) were recorded in Swale soils. Samples obtained from Tombia showed highest values of Fluoranthene (33.09µg/kg) and Indeno(1,2,3 cd)pyrene (38.31µg/kg). Swale recorded highest concentration of total PAHs which was followed by Tombia, Igbogene, Opolo while Azikoro (control) had the least values of PAHs components.





Result of the assessment of the total PAHs in the samples is presented in Figure 2. It shows that soil from Swale abattoir had the highest PAHs contamination ($625.48\mu g/kg$).

While the least value was obtained at the Opolo abattoir (138.06 μ g/kg). The Total PAHs in abattoir soil samples based on location had the order: Swale > Tombia > Igbogene > Opolo > Azikoro (control).





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The six heavy metals assessed in abattoir soils include Pb, Cd, Cr, Ni, Hg and Fe. The obtained values are presented in Figures 3a and 3b. Fe had the highest concentration values at all locations. The highest values of Pb (21.67mg/kg), and Fe (857.4mg/kg) were recorded in Tombia soil. Swale recorded highest value of 6.08mg/kg in Cd, Opolo soil samples were highest

in Cr and Ni with 8.65 and 9.66mg/kg values respectively. Hg was undetected in all the soil samples. Also, heavy metal values were lowest in Azikoro, the control sample. The decreasing order of the concentration of heavy metals detected in soil samples is: Fe > Pb > Ni > Cr > Cd. Cr>Hg.

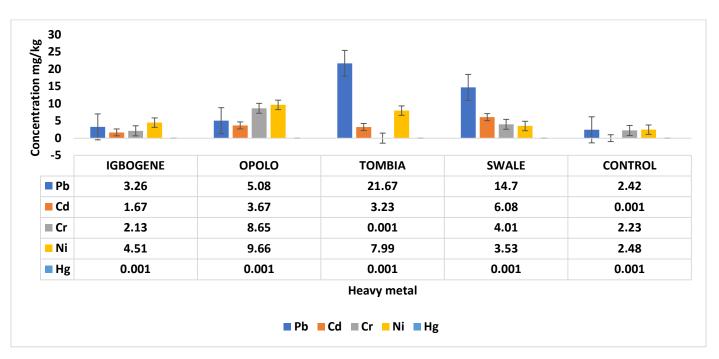


Figure 3a: Heavy metal content of abattoir soils

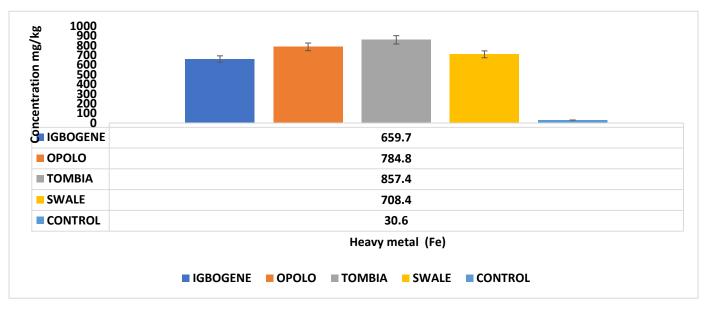


Figure 3b: Heavy metal (Fe) content of abattoir soils

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Discussion

Assessment of abattoir soil samples for contamination by deposition of PAHs, indicated that the soil in all the abattoirs had polycyclic aromatic hydrocarbons contamination. This evaluation showed that low molecular weight polycyclic aromatic hydrocarbons Acenaphthene and Acenaphthylene like were undetected in all the abattoir soils examined. Furthermore, PAHs with low molecular weight are more water soluble, less lipophilic, more volatile and thus less recalcitrant compounds while the higher molecular weight PAHs show higher hydrophobicity and lipophilicity (Mackay et al., 1992; Okere and Semple. 2012). Anthracene. Benzo(a)anthracene. Benzo(a)pyrene, Benzo(b)fluoranthene and Chryesene were highest in Igbogene soil sample. Benzo(g,h,i) Benzo(k)fluoranthene, Dibenz(a,h) pervlene. anthracene, Fluorene, Naphthalene, 2methylnaphthalene, Phenanthrene and Pyrene were seen to be highest in Swale abattoir soil sample. Fluoranthene and indeno(1,2,3,cd) pyrene were highest in Tombia abattoir soil sample. The detected values of Pyrene were relatively highest among the entire individual PAHs assessed in all the stations.

Furthermore, the highest pyrene value was recorded in Swale soil samples. However, the concentrations of Benzo(a)pyrene (marker for PAHs carcinogenicity) had concentrations above the WHO permissible limit of 5µg/kg in Igbogene and Swale samples. Swale soil recorded the highest values of individual PAHs This is unconnected with the fact that this abattoir has the largest slaughtering capacity and activity. The values of PAH4 were all significantly high in all soil samples. Individual PAHs such as Pyrene, Benzo(b) flouranthene, Flouranthene, Indenol (1,2,3cd)pyrene and Naphthalene were all recorded in high concentrations in abattoir soils in this study. This is indicative of the fact that PAHs have been accumulating in the abattoir soil over time consequent to routine abattoir activities.

These individual PAHs are all classified as probable human carcinogen thus confirming the possibility of human health hazard from abattoir locations. High molecular weight PAHs (PAHs with four or more aromatic rings) are considered to be more hazardous than those with two and three rings PAHs because of their higher genotoxic potentials. Jones *et al*, 1989 recorded PAHs in substantial and consistent increase in PAHs content of soil profile samples collected from the same plot at Rothamsted Experimental Station in Southeast England in 1893, 1944 and 1987. They confirmed atmospheric deposition of PAHs and its increase over this duration of time to be due to anthropogenically generated largely from the combustion of fossil fuels. Furthermore, PAHs known for acute carcinogenic, mutagenic and teratogenic properties such as benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*a*] pyrene, benzo[*g*,*h*,*i*]perylene, chrysene, dibenz(a,h) anthracene, indeno(1,2,3-cd)pyrene (Luch, 2005; Xue, and Warshawsky, 2005) were found in abattoir soils.

The total PAHs value in sampled stations was highest in Swale (625.48µg/kg). Aside the fact that this abattoir has the largest slaughtering capacity, singeing of cowhide was also carried out with open fire made with expired tyres and plastics. This may be responsible for it recording the highest PAHs value. The study carried out by Ariyo and Obire, 2023, confirmed a higher concentration of PAHs in the soil of Rupokwu abattoir where animal skin dressing was carried out with open fire from tyre flaring. Even though other abattoir recorded varying concentrations of total PAHs, the least value was recorded in the control soil. This confirms that anthropogenic activities in the abattoirs are generating PAHs and they are deposited unto the environment. PAHs strongly adsorbed onto soil particles, and therefore, the soil ecosystem becomes an ultimate sink for them. The total PAHs concentrations in all the soils were below the EU permissible limits of 1000µg/kg in soils. Nevertheless, there is need for constant monitoring of abattoir activities in order to avert possible health and hazard risks.

Heavy metals occur in the environment naturally and are further released during anthropogenic activities. Soil contamination with heavy metals results from human-related activities such as mining (Navarro, et al., 2008), smelting procedures (Brumelis et al., 1999) and agriculture (Vaalgamaa and Conley, 2008) as well as earth-related activities. Heavy metals pollution has been a source of concern because of their persistence in environment. their toxicity and their the bioaccumulation ability. Heavy metals assessed in soil and wastewaters include Pb, Ni, Cr, Cd, Hg, Ni and Fe. Out of all the metals examined only Hg was not detected in the abattoir soils.

The heavy metal that recorded the highest concentration in soil is Fe which was detected in Tombia soil sample. Study conducted by Osu and Okereke, 2015, also recorded Fe in the highest concentration among all the heavy metals they evaluated in Umuahia abattoirs soils. Ubwa *et al.*, 2012, reported varying concentrations of Zn, Pb, Ni, Cr and Cd in Gboko abattoir soils.

In conclusion, this study indicated higher concentration of polycyclic aromatic hydrocarbons and heavy metal contamination levels detected in all the abattoir soil samples assessed than in the control. This is suggestive that the abattoir soils were contaminated due to ongoing anthropogenic activities (slaughtering and bleeding the animals, dumping of untreated gut wastes on the soil, roasting of cowhide for meat with open fires making use of various organic fuel sources etc.) in the abattoirs. Processing and dressing of meat in these abattoirs are yet being carried out in an unregulated manner. Modern slaughterhouse facilities are still not available. Government through relevant agencies should assist to make available modern meat processing facilities and also set up waste treatment plant in the abattoirs to prevent the indiscriminate discharge of untreated wastes (and its implications) onto the soil which may pose a risk to human health as well as microorganisms that are inhabitant of the environment.

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