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Comparative Effect of Firewood and Automobile Tyre Flaring on Polycyclic Aromatic Hydrocarbons (PAHs) and Heavy Metal content of Abattoir Soils in Rivers States

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Abstract: Soils around the vicinity of two Abattoirs located in Obio/Akpor Local Government Area of Rivers State were collected and analyzed for Polycyclic aromatic hydrocarbon and heavy metals using standard methods. Rukpokwu abattoir is noted for roasting/processing cowhide for meat exclusively with expired automobile tyres as fuel source while firewood is exclusively being used at Rumuokoro abattoir. Levels of polycyclic aromatic hydrocarbons (PAHs) in the sample were determined using Gas chromatographic method, while the heavy metals were determined using spectrophotometer. Roasting activities were carried out in Rupokwu abattoir by flaring expired tyres while firewood is used in Rumuokoro abattoir for same. Results of the individual PAHs in abattoir soils indicated the absence of low molecular weight members such Acenaphthene and Acenaphthylene however Naphthalene was recorded. Rukpokwu recorded higher value of 4.78µg/kg for Anthracene while the least value of 0.36 µg/kg was observed in the control. Benzo(a)anthracene and Phenanthrene were only recorded in Rukpokwu. Chrysene and Fluoranthene were obtained from Rupokwu and the control. Benzo(a)pyrene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Benzo(k)fluoranthene, Dibenz(a,h)anthracene, Indeno(1,2,3cd)pyrene, Fluorene, Naphthalene, 2-methylnaphthalene and Pyrene recorded higher values of 10.75, 19.21, 14.49, 156.99, 39.55, 30.03, 39.3, 26.25 and 290.17µg/kg in Rukpokwu. The total concentration of PAHs was more in Rukpokwu than Rumuokoro soil with significant difference ($P<0.05$). Rukpokwu soil recorded the higher values of (36.74, 10.2, 10.98, 13.53, 744.6) mg/kg for Pb, Cd, Cr, Ni and Fe, respectively. This is not unconnected with the cowhide charring carried out with tyre fire in this abattoir. It was generally observed that PAHs concentrations in all the soils were below the EU permissible limits of 1000µg/kg in soils. However, continual monitoring of slaughterhouse operations that can result in the disperse and deposit of PAHs and heavy metals into the air and soil is required to reduce the potential threats to human health and safety.

Keywords: Abattoir, Tyre Fire, Firewood, Polycyclic Aromatic Hydrocarbon, Heavy Metals, Gas Chromatography

1. Introduction

An abattoir is where the butchering of animals and preparing of meat items for human utilization is performed. Activities in abattoir generate large volume of wastes which are discharged improperly to the environment. The wastes generated from abattoir have been reported to have negative impact on the receiving environment [1]. A variety of organic fuels sources are being utilized for the roasting/processing of meat, fish and cowhide. These include animal dung (in some countries) to corn cobs, through a variety of soft and hard woods. Within the Niger delta region, organic fuel used for roasting fishes include firewood, bamboo, saw dust, palm fruit chaff, grass straw, coconut husk among others. Also, fuel sources being flared for roasting cowhide in Rivers state include expired automobile tyres, firewood, waste plastics, kerosene to mention a few. Since there is considerable variation in the composition of various fuels, the components of smoke vary widely. The reactions involved in production of smoke and its components will depend largely upon individual fuels and their composition [2].

When these fuel sources are flared, they produce smoke. Smoke is a complex compound with approximately 400 components, many of which are harmful to human health [3, 4]. The gases released from burning tyres in the open are filled with hazardous substances such as volatile organic compounds, heavy metals, PAHs, dioxins, and furans, making them very detrimental to human health. Many researchers have affirmed that abattoir waste can affect soil health; reduce biodiversity; influence human wellbeing; and contaminate the air, water, and soil with harmful polycyclic aromatic hydrocarbon and heavy metals [5]. The ubiquitous nature of PAHs in the environment [6], if deposited and stored in soils, it becomes a major human and ecosystem health concern owing to their proven carcinogenicity and potential toxicity to both aquatic and terrestrial creature [7]. Observation of PAHs in areas far from direct emission or production help researchers understand the impact of air transport on ecosystem integrity. Meat processing procedures such as burning animal bones and skin with tyres, wood, plastic, or coal emit smoke and gases into the environment thus polluting the air [8]. Pollutants emitted in gas flares gradually settle down as a result of dissolution in rainwater or binding to airborne particles and soil eventually serves as the sink. Several studies, including those conducted by [9-12], have identified atmospheric PAHs deposition as a major contributor to PAH contamination in soil. Consequently, open-air flaring for a variety of meat processing techniques in abattoir is still common in developing countries such as Nigeria. This aspect of abattoir activity can also introduce chemical pollutants such as polycyclic aromatic hydrocarbons (PAHs) and others to the environment [8]. Wastes from abattoir are deposited onto the ground or channeled into water resources due to lack of waste treatment facilities, resulting in environmental pollution. It has also been established that natural wastes from slaughterhouses can increase the level of Fe, Pb, and Zn in the environment. Harmful metals have been discovered in blood, hair, and most organs of steers [1]. According to some scientists, abattoir wastes have the potential to significantly alter the physicochemical properties of soil considerably. In this study, the soil within some abattoirs in Rivers State were tested for PAHs and heavy metal deposits based on the type of fuel source being flared for animal processing.

2. Materials and Methods

2.1. Sampling Location

Samples for this study were collected from two abattoirs located in Rumuokoro and Rukpokwu towns both in Obio/Akpor Local Government Area of Rivers State. Control samples were collected from Azikoro (Bayelsa), a community with no record of abattoir activity as at the time of sampling for this study. The map coordinates of the abattoir locations are as stated in Table 1.

Table 1. *Sample Locations and their Coordinates.*

Location	Northing (N)	Easting (E)	Cowhide roasting fuel type
Rumuokoro	4^0 52’ 11.64”	7^0 01’ 026”	Firewood
Rukpokwu	4^0 57’ 10.908”	6^0 21’ 20.7432”	Expired automobile tyres
Azikoro (Control)	4^0 57’ 13.77”	6^0 21’ 19.5048”	No flaring activity

2.2. Sample Collection

Soil samples (500g) made up of three composite samples was collected from each abattoir as well as the control site with the aid of a hand soil auger at about 0-15cm depth. Soil samples were transported to the laboratory in ice packs and stored in the refrigerator for analyses.

Sample preparation: Soil samples were air-dried to constant weight at room temperature for few days, crushed to smoothness with mortar and pestle and sieved through a 2mm wire mesh.

Sample extraction: Two grams of each solid matrix sample was weighed into a clean extraction container separately and 10ml of Dichloromethane was added into each and mixed thoroughly by stirring with glass rod and filtered through cotton wool stuffed filter funnel into clean solvent rinsed extraction bottles. This extract was concentrated to 2ml by evaporating on a water bath at 40°C.

2.3. Sample Cleanup/Separation

One cm of moderately packed glass wool was placed at the bottom of a 10mm I.D. x 250mm long chromatography column. Slurry of 2g activated silica gel in 10ml dichloromethane was prepared and placed into the chromatography column. To the top of the column was added 0.5cm of anhydrous sodium sulphate. The column was rinsed with additional 10ml of Dichloromethane. The column was pre-eluted with 20ml of Dichloromethane; this was allowed to flow through the column for about 2 minutes until the liquid in the column was just above the anhydrous sodium sulphate layer. Immediately, 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. Accurately measured volume of 8-10ml of the eluent was collected and labeled ‘ALIPHATICS’. Following the recovery of the aliphatics fraction, the column was eluted with 1:1 mixture of propanol and Dichloromethane in 1-2ml increments. Another accurately measured 8-10ml of the eluent was collected and labeled 'AROMATICS'. The aromatic fraction was concentrated to 1ml for PAHs analysis before being injected into the Gas Chromatograph.

2.4. Measurement of Polycyclic Aromatic Hydrocarbons

The Polycyclic Aromatic Hydrocarbon (PAHs) content of samples were determined through the principle of Gas Chromatography by flame ionization detection as sample extracts are being forced through an immobile, inert stationary phase (1,3-dimethyl siloxane) and components of low solubility take a shorter time to be transported through the column while components of higher solubility take a longer elution time leading to the differential mobilities of the fractional components of the polycyclic aromatic hydrocarbons (PAHs). 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 specification of the Gas Chromatography used is as stated below:

Equipment used: HP 5890 Series II GC, U.S.A.

The operational condition (temperature program) for the GC analysis is stated below:

Injection temperature:
Initial oven temperature = 60°C
Actual oven temperature = 275°C
Detection temperature = 300°C
Capillary column: 30m length, 0.32mm internal diameter
Detector: Flame Ionization Detector.

2.5. Reagent(s)

(a) PAH Standard for GC calibration: Restek SV Calibration Mix No 5 2,000ug/ml each in Methylene Chloride, 110 Benner Circle Bellefonte. PA 16823.
(b) Dichloromethane (BDH Laboratory reagents), BDH Chemicals Ltd, England.
(c) Silical Gel (Bourgoyne & Co. Reagent, Mumbai, India).
(d) Anhydrous Sodium Sulphate (SureChem Products Ltd, Suffolk, England).

2.6. Gas Chromatography Analysis

The concentrated 'AROMATICS' extracts were transferred into labeled glass vials with Teflon Rubber Crimp cap for GC analysis. One microlitre (1µl) of the concentrated sample was injected by means of a hypodermic syringe through a rubber septum into the column. Separation occurs as the vapour constituent partition between the gas and the liquid phases. The constituent aromatic compounds are automatically detected as it emerges from the column (at a constant flow rate) by the Flame Ionization Detector whose response is dependent upon the composition of the vapour, by measuring the detection time.

The GC was calibrated by calibration curve method using standard solutions (working concentration of 50, 100, 200 and 1000mg/l PAH mixture by AccuStandards).

2.7. GC Operation Condition

Initial oven temperature = 65°C
Rate: 25°C /minute (actual) = 140°C
Rate: 10°C /minute (final) = 300°C
Run time = 44minutes.

2.8. Determination of Heavy Metals

Assessment for heavy metals was carried out using the atomic absorption spectrophotometric method of A.P.H.A [13].

Procedure: 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 HNO_3 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. The beaker was removed from hot plate when the solution was remaining 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.

3. Results

3.1. Mean Concentration of Individual PAHs in Soil

Figures 1 and 2 show the individual polycyclic aromatic hydrocarbons analyzed from the soil samples obtained from Rumuokoro (an abattoir making use of firewood as fuel source for roasting) and Rukpokwu (an abattoir making use of expired automobile as fuel source for roasting). The control soil sample was collected from Azikoro (a site with no abattoir activity as at the time of sampling) in Bayelsa State. Assessment of PAHs in abattoir soils indicated the absence of low molecular weight members such Acenaphthene and Acenaphthylene however Naphthalene (with 2 benzene rings) was recorded in all the soil samples. However, the concentration was highest at the tyre flaring site (39.30 µg/kg), followed by the firewood flaring site (10.04 µg/kg) and least at the control site (4.31 µg/kg). Rukpokwu soil recorded highest value of 4.78µg/kg for Anthracene while the least value of 0.36µg/kg was observed in the control. Benzo(a)anthracene and Phenanthrene were only recorded in Rukpokwu soil. While Chrysene and Fluoranthene were not recorded at the firewood flaring abattoir (Rumuokoro), they were found at the tyre flaring abattoir (Rukpokwu) and the control site, at 3.62µg/kg and 1.16µg/kg for Chrysene and 4.37µg/kg and 2.94µg/kg for Fluoranthene respectively. In the tyre flaring abattoir, concentrations of Benzo(a)pyrene, Benzo(g,h,i)perylene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Dibenz(a,h)anthracene, Indeno(1,2,3cd)pyrene, Fluorene, Naphthalene, 2-methylnaphthalene and Pyrene recorded highest values of 10.75, 19.21, 14.49, 156.99, 39.55, 30.03, 39.3, 26.25 and 290.17µg/kg respectively and least values in the control sample. The concentration of total PAHs was more in Rukpokwu than Rumuokoro. The control recorded the least concentration of total PAHs as shown in Table 2.

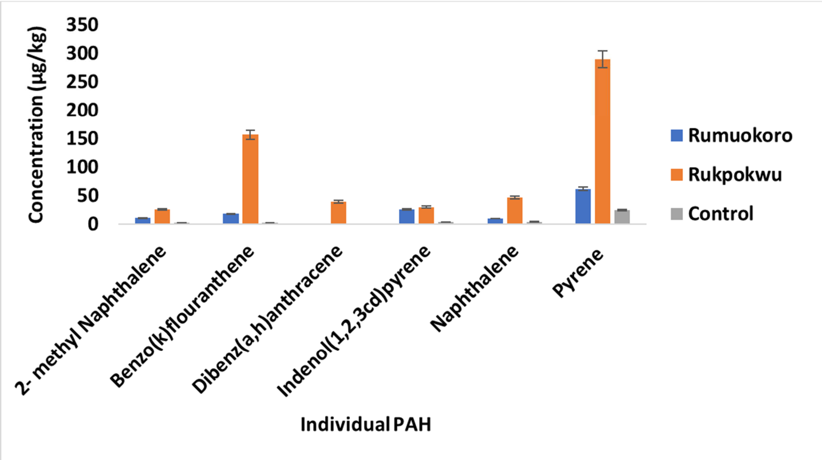

Figure 1. *Concentration of individual PAHs in abattoir soils.*

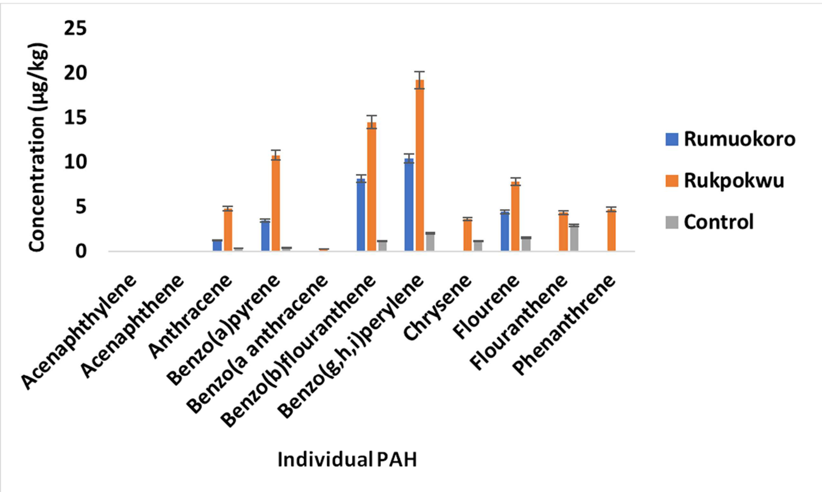

Figure 2. *Concentration of individual PAHs in abattoir soils.*

Table 2. *Total Concentration of PAHs in abattoir soils.*

Location	PAHs (µg/kg)	Roasting fuel source
Rumuokoro	99.64	Firewood
Rukpokwu	652.40	Expired tyre
Azikoro (Control)	47.91	Flaring activity

3.2. Heavy Metals in Soil Samples

The six heavy metals assessed in abattoir soils include Hg, Ni, Pb, Cr, Cd and Fe. All the metals were recorded in varying concentrations in the soil samples. The obtained values are presented in Table 3. Rukpokwu recorded the highest values of 36.74, 10.2, 10.98, 13.53, 744.6 mg/kg for Pb, Cd, Cr, Ni and Fe, respectively. While the concentrations of metals were lower in Rumuokoro soil sample the least values were obtained in the control soil.

The decreasing order of the concentration of heavy metals in soil samples is Fe > Pb > Ni > Cr > Cd.

Table 3. *Heavy Metal Content.*

Heavy Metal	Rumuokoro (mg/kg)	Rukpokwu (mg/kg)	Control (mg/kg)
Pb	32.25	36.74	2.42
Cd	2.5	10.3	0.001
Cr	6.03	10.98	2.23
Ni	11.35	13.53	2.48
Hg	0.001	0.001	0.001
Fe	727.3	744.6	30.6

4. Discussion

The purpose of this study was to see what effect roasting fuel type had on polycyclic aromatic hydrocarbons and heavy metals in soil samples from Rumuokoro and Rukpokwu abattoirs in Rivers state. The research will also compare the effect of roasting fuel (firewood and tyres) on the deposition of these pollutants into abattoir soils. Low molecular weight PAHs such as acenaphthene and acenaphthylene were found in none of the soil samples. However, naphthalene (a PAH with only two benzene rings) was found in high concentrations in all soil samples tested. This corroborates the findings of Essumang [14], who discovered low molecular weight PAHs at the Oblogo dumping site in Ghana.

When PAHs are released into the environment, the majority of naphthalene is retained in the air and soil for a shorter period of time (half-lives in the soil are typically a few hours) before being degraded. The ability of low molecular weight PAHs to be easily degraded via photooxidation may explain why they were not detected in samples. Nonetheless, the presence of naphthalene at relatively high concentrations in abattoir soil samples indicates constant, current, and continuous deposition as flaring activities were ongoing. Individual PAH results revealed that soils in Rukpokwu abattoir where expired automobile tyres were used to roast cowhides had the highest levels of anthracene, benzo(a) anthracene, phenanthrene, chrysene, fluoranthene, benzo(g,h,i) perylene, benzo(k)fluoranthene, and dibenz(a,h)anthracene. The presence of significantly higher total PAHs in abattoir soils than in control soil sample is an indication that abattoir activities have impacted these pollutant deposits on the soil away from the source of emission. The total PAHs concentration was higher in Rukpokwu abattoir soil than in Rumuokoro abattoir soil. This indicates that polycyclic aromatic hydrocarbons have accumulated in the abattoir soil over time consequent to routine abattoir activities. This is due to the total PAHs concentration in the control sample is much lower than in the abattoir soil samples. Rukpokwu abattoir is an abattoir dedicated exclusively to burning cowhide for meat by roasting it with expired car tyres. This type of fuel source may be responsible for the soil recording the higher PAH value. A lower total PAH value was recorded in Rumuokoro abattoir soil. This is not unrelated to the fact that tyre flaring for roasting cowhide is not permitted in this particular abattoir; instead, cowhide is processed by roasting with firewood. In addition, government agencies are closely monitoring this abattoir for compliance. The occurrence of PAHs in the control sample (Azikoro) suggests that particulates are transported from distant sources of emission to locations where they are deposited [15]. However, the total PAH concentrations detected in all the soils are below the EU permissible limits of 1000μg/kg in soils. Nevertheless, constant monitoring of abattoir activities in required to avoid potential health and safety risks. Heavy metals tested in abattoir soils include Pb, Ni, Cr, Cd, Hg, Ni, and Fe. There was no trace of Hg found in the abattoir as well as control soils. Fe is the heavy metal that recorded the highest concentration in the soil samples. This study corroborates that of Osu and Okereke [16] who found the highest heavy metal concentration in Fe among all the heavy metals they tested in Umuahia abattoirs. They also recorded varying concentrations of Fe, Cd and Pd however the concentrations recorded in Umuahia abattoir soil however in lower concentrations than what was obtained in this study. This implies that the heavy metal concentrations in abattoir soil samples may vary depending on sampling sites, soil composition and the volume of human activities within the abattoir.

The report of this research study agrees with that of Chimezie [17] on the incidence of increased heavy metal contamination of the environment due to industrial and/or anthropogenic activities. Ubwa [18] reported varying concentrations of Zn, Pb, Ni, Cr, and Cd in Gboko abattoir soils. A study conducted by Nawrot et al. [19] found a significant relationship between cadmium concentration in the soil, or residence in a high-exposure area, and lung cancer even after adjustment for age, sex, smoking, and exclusion of cadmium-exposed workers. The presence of Pb, Ni, Cr, and Cd in soils has been reported by many researchers including Osakwe and Okoli [20], Osu and Okereke [16] as well as Kalu and Anaga [21].

5. Conclusion and Recommendation

The study showed that polycyclic aromatic hydrocarbon and heavy metal were present in the soil within the abattoirs in the locations sampled. The result further indicated that soil in the abattoir where used tyres were being flared for the roasting of cowhide and other abattoir processing activities recorded higher concentration of pollutants. This continuous discharge of abattoir wastes and burning activities during the procedures of meat processing could have been responsible for the occurrence of high pollutant load. The use of open fire(s) in abattoirs for the preparation of meat and fish products is of hazardous to health concerns. It contributes largely to air, soil and food pollution. This is largely owning to the fact thermal combustion produces/releases smoke which is a complex compound containing variety of compounds, including PAHs, which are classified as probable human carcinogen implying that there is a risk to human health.

In conclusion, relevant regulatory agencies should actively supervise routine slaughter house activities in the course of processing killed animals as meat for human consumption. Additionally, abattoir wastes should be handled in such a manner that they can be treated before being discharged to the environment.

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