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Polycyclic Aromatic Hydrocarbons (PAHs) and Heavy Metal content of Abattoir Wastewater in Bayelsa and Rivers States

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Abstract

The polycyclic aromatic hydrocarbons and heavy metals in wastewater generated from abattoir were analyzed. Wastewater samples were collected from four abattoirs in Yenagoa Local Government Area of Bayelsa State and an abattoir in Obio/Akpor Local Government Area of Rivers State, respectively using standard methods. The polycyclic aromatic hydrocarbons (PAHs) were determined using Gas chromatographic method, while the heavy metals were determined using spectrophotometer. Results showed that Acenaphthene, Acenaphthylene and Naphthalene recorded its highest value of 123.77µg/ml, 199.64µg/ml and 6.82µg/ml, respectively in wastewater samples from Opolo, while they were not detected in Rumuokoro samples (0.00µg/ml). Anthracene recorded the highest value in sample from Opolo (4.59 µg/ml) and the least value was in samples from Swale (0.00 µg/ml). Values of Benzo(a)pyrene recorded value of 0.86 µg/ml in Opolo sample. Chrysene value was 66.19µg/ml in Rumuokoro wastewater, 0.03µg/ml in Igbogene wastewater and 0.24 µg/ml in the control while the value was 0.00µg/ml in other abattoir locations. Benzo(b)flouranthene recorded the highest value of 38.79µg/ml at Igbogene and 1.93µg/ml in Tombia while other sampling location recorded 0.00µg/ml. Indenol(1,2,3cd) pyrene highest value of 4.38µg/kg was obtained at Igbogene, Swale, and the control, recorded zero value. Flourene was present in all the abattoir samples but with the highest concentration at Opolo (42.96µg/ml) and the least concentration in Swale (0.17µg/ml). The highest value of 2-methylnaphthalene recorded was 52.65µg/ml at Opolo which was followed by 11.2 µg/ml at Tombia while it was not detected in other locations (0.00µg/ml). Flouranthene recorded its highest concentration of 55.01µg/ml (Rumuokoro) and the least were 0.00µg/ml at Tombia. Rumuokoro and Igbogene had Benzo (k) fluoranthene concentrations of 14.90g/ml and 0.02g/ml, respectively, whereas other locations had zero. Except for Anthracene, Fluoranthene, Pyrene, Chrysene and Benzo(g,h,i)perylene, all the other PAHs were not detected in the control. The decreasing order of total PAHs in wastewater samples is as: Opolo > Tombia > Rumuokoro > Igbogene > Swale > Control. Chromium (Cr) was detected in wastewater from all abattoir locations, while all other heavy metals were undetected. Results from this study shows that the abattoir wastewaters had high pollution strength and thus should be treated before being discharged into the environment. The presence of PAHs that are known carcinogens poses a serious threat to the health and well-being of humans.

Keywords: Abattoir wastewater, PAHs, Benzo(a)pyrene, Benzo(b)flouranthene, Heavy metals, Pollution strength.

1. Introduction

An abattoir is a place where animals are being slaughtered and processed for human consumption (Atuanya *et al*., 2012; Hornby, 2006). Activities in abattoir generally result in the generation of a high volume of wastes which are not managed and discharged properly (Osibanjo and Adie, 2007). In Africa, reports have shown that these wastes have a high potential of negative impact on the receiving environment (Nwachukwu *et al*., 2011; Mohammed and Musa, 2011; Neboh *et al*., 2013). In Nigeria, the abattoir industry is an important component of the livestock industry providing domestic meat supply to over 150 million people and employment opportunities for teaming population. However, the abattoir industries are less developed in developing countries like Nigeria. Facilities for the treatment of abattoir effluents are lacking, unlike in developed countries where these facilities are adequately provided (Ogbonnaya, 2008). Potential health risks from waterborne pathogens can exist in water contaminated by abattoir effuents (Kosamu *et al*., 2011), runoff from feedlots, dairy farms, grazed, fallow and sod amended with poultry litter, grassland treated with dairy manure, and sewage sludge treated land (Kosamu *et al*., 2011). Also, polycyclic aromatic hydrocarbons and heavy metals can be found in the wastewater. Such contamination of water bodies from abattoir wastes could constitute significant environmental and public health hazards (Osibanjo and Adie, 2007). Abattoir wastewater is a typical source of pollution and are of serious environmental concerns. Abattoir operations produce characteristic highly inorganic wastes such as sulphates, phosphates, etc. with relatively high levels of suspended solid, liquid and fat. The solid waste includes condemned meat, undigested food materials, bones, hairs and aborted fetuses. The liquid waste is usually composed of dissolved solids, blood, gut contents, urine and water (Ojo *et al*., 2012). As a result of inadequate waste treatment facilities, wastes from abattoir are deposited on the land or channeled into water resource leading to pollution. Abattoir wastewater has a complex composition and is very harmful to the environment, (NIS, 2007). It is strong compared to domestic wastewater. It may also contain some manure. Such characteristics render abattoir wastewater treatment very difficult, (Bohdziewicz and Sroka, 2005). Because of lack of adequate abattoir facilities in developing countries like Nigeria, abattoirs are usually sited close to water bodies like rivers to enable easy discharge of generated (usually untreated) wastes into the rivers. Wastewaters generated from these abattoirs are being discharged into river. There was therefore the need to determine the level of polycyclic aromatic hydrocarbon and heavy metals generated from these abattoirs' wastewater, which would provide data needed to inform operators of the abattoirs, users of the river and the general public on the level of pollution generated. The data generated will also assist the government in enacting policies that will ensure wholesome abattoir practices and thus protect public health.

2. Materials and Methods

Sampling Location

Samples for this study were collected from four abattoirs in Yenagoa Local Government Area of Bayelsa State and an abattoir in Obio/Akpor Local Government Area of Rivers State. Water samples which were not polluted by abattoir activities were also collected from Tombia in Bayelsa State. These unpolluted water samples served as control for this study.

The map coordinates of the abattoir locations is as stated in Table 1.

Table 1: Sample Locations and their Coordinates

Location	Northing (N)	Easting (E)
Igbogene	5^0 2' 17.8188"	6^0 24'14.958"
Tombia	4^0 57' 17.8092"	6^0 20'53.2428"
Opolo	4^0 56'52.764"	6^0 20'3.984"
Swale	4^0 53'42.9576"	6^0 16'39.7164"
Rumuokoro	4^0 52' 11.64"	7^0 01' 026"
Tombia (Control)	4^0 57' 17.8092"	6^0 20'53.2428"

Sample Collection

Wastewater produced after washing of the roasted cowhide of the slaughtered animals was collected from drainages along three sampling points in each abattoir into 1.5litre sterile bottles. This was also prepared into a composite sample. Wastewater samples were collected using the method of Adesemoye *et al.* (2006). The samples were collected at three different points as the waste water was running off the drains. About 500ml of sample water was collected from each point and were pooled together to constitute a composite sample.

Sample extraction: Two hundred and fifty (250 ml) of wastewater was measured into flasks and 25ml 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 40^0C.

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.

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 ^{0}C
Actual oven temperature = 275 ^{0}C
Detection temperature = 300^{0}C
Capillary column: 30m length, 0.32mm internal diameter
Detector: Flame Ionization Detector
Reagent(s)
(a) PAH Standard for GC calibration: Restek SV Calibration Mix No 5 2,000µg/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)

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).

GC Operation Condition

Initial oven temperature	=	65^{0}C
Rate: 25^{0}C/minute (actual)	=	140^{0}C
Rate: 10^{0}C/minute (final)	=	300^{0}C
Run time	=	44minutes

Chemicals and Reagents Used

All the reagents used for these analyses are of analytical grade and are products of Eagle Scientific Limited, England, BDH Limited, England, Surechem Products Ltd, England, Rieldel-De Haen, Germany, Sigma-Aldrich, Germany, Kermel, China and Burgoyne Burbridges, India.

Determination of Heavy Metals

Atomic Absorption Spectrophotometric method of A.P.H.A (1998) was used.

Wastewater sample of 20ml was measured into 250 ml beaker to which 1:10 v/v mixture of HNO3 and HCl was added. The mixture was concentrated to 5ml by boiling on hot plate at 95^{o}C
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

Mean Concentration of individual PAHs in Wastewater

The results of assessment of abattoir wastewater samples were assessed for the 17 priority PAHs are presented in Figures 1 while Figure 2 is showing the Total PAHs concentration from the samples. Low molecular weight members such as Acenaphthene, Acenaphthylene and Naphthalene were detected in wastewater sample at varying relatively high concentrations. That Acenaphthene, Acenaphthylene and Naphthalene recorded its highest value of 128.77µg/ml, 199.64µg/ml and 6.82µg/ml, respectively in wastewater samples from Opolo, while their least values of 0.00µg/ml was detected in Rumuokoro samples. Anthracene recorded the highest value in sample from Opolo (4.59 µg/ml) and the least value was in samples from Swale (0.00µg/ml). Values of Benzo(a)pyrene recorded value of 0.86µg/ml in Opolo sample. Chrysene value was 66.19µg/ml in Rumuokoro wastewater, 0.03µg/ml in Igbogene wastewater and 0.24 µg/ml in the control while the value was 0.00µg/ml in other abattoir locations. Benzo(b)flouranthene recorded the highest value of 38.79µg/ml at Igbogene and 1.93µg/ml in Tombia while other sampling location recorded 0.00 µg/ml. Indenol(1,2,3cd) pyrene highest value of 4.38µg/kg was obtained at Igbogene, Opolo, Swale, and the control, recorded zero value. Flourene was present in all the samples but with the highest concentration at Opolo (42.96µg/ml) and the least concentration in Swale (0.17µg/ml). The highest value of 2-methylnaphthalene recorded was 52.65µg/ml at Opolo and 11.22µg/ml at Tombia while other locations recorded concentration values of 0.00µg/ml. Flouranthene recorded its highest concentration of 55.01µg/ml (Rumuokoro) and the least were 0.00µg/ml at Tombia. Concentrations of Total PAHs from the stations are; Opolo 450.61µg/ml, Tombia 246.61µg/ml Rumuokoro - 146.23µg/ml, Igbogene - 44.02µg/ml, Swale - 29.04µg/ml and Control - 0.66µg/ml. Consequently, the decreasing order of mean concentration of total PAHs in wastewater samples is as: Opolo > Tombia > Rumuokoro > Igbogene > Swale > Control.

Statistical analysis for significant difference indicated that the total PAHs concentrations of all the samples are significantly different when compared with the control. However, there is no significant difference in the total PAHs values on contamination of wastewater between Igbogene and Swale. However, there are significant differences in the total PAHs values on contamination of wastewater across other selected locations.

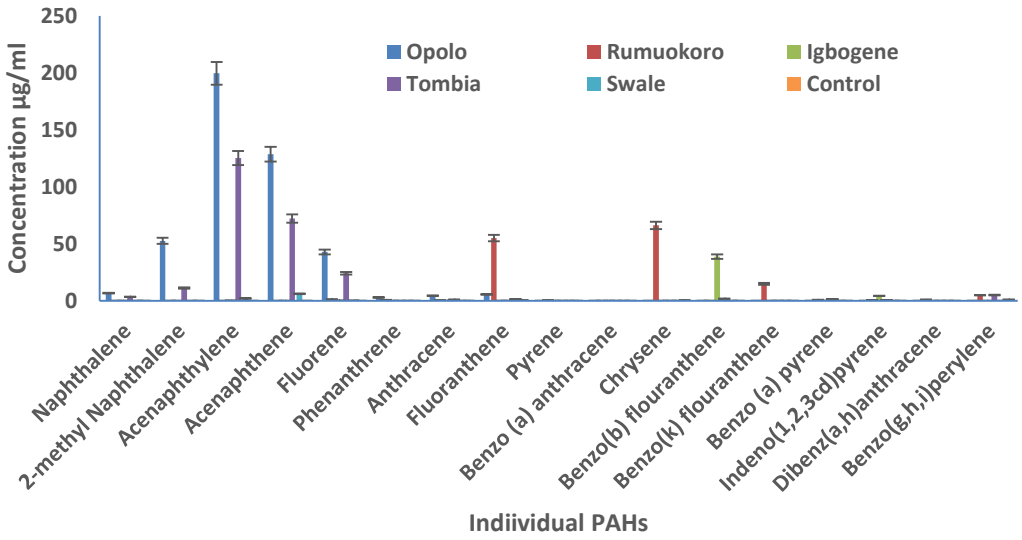

Fig. 1: Concentration of Individual PAHs in Abattoir Wastewater

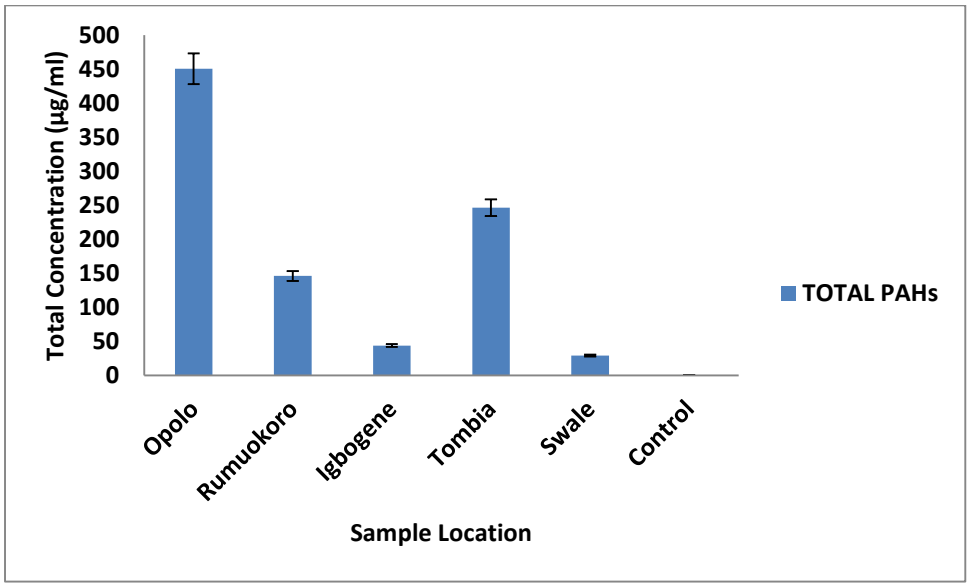

Figure 2: Total Concentration of Total PAHs in Abattoir Wastewater

Mean of Heavy metals in Wastewater

Heavy metals examined in wastewater samples obtained from abattoirs include Pb, Cd, Cr, Hg, Ni and Fe. Cr was detected in wastewater from all abattoir locations, while all other heavy metals assessed was undetected, Fe that was not assessed in wastewater samples (Fig. 3). The value of Cr obtained from all the abattoir locations are: Igbogene – 0.84mg/l, Opolo – 0.56mg/l, Rumuokoro – 0.59mg/l, Tombia – 0.4mg/l and Swale – 0.58mg/l.

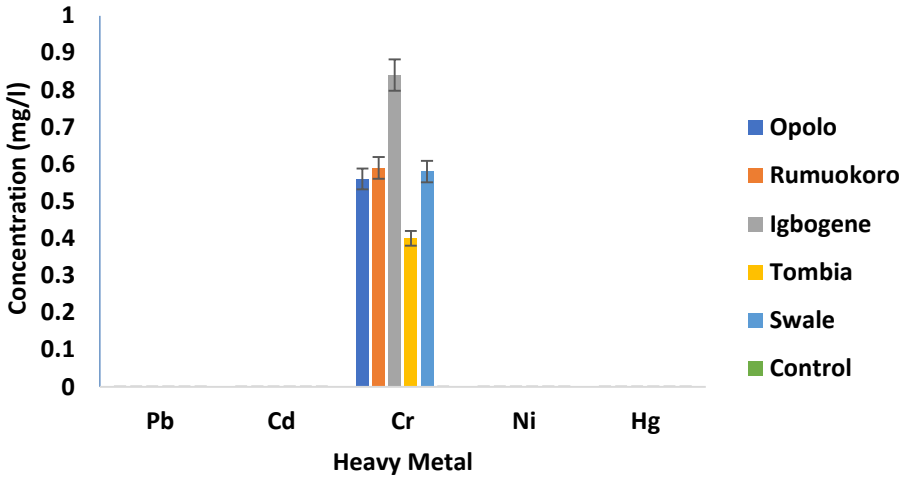

Fig. 4: Mean concentration of Heavy Metals in Wastewater Samples

4. Discussion

This study was conducted to determine the polycyclic aromatic hydrocarbons (PAHs) and heavy metals contents of some abattoir wastewater in Bayelsa and Rivers States. Seventeen individual PAHs were analyzed from the wastewater samples. Except for Anthracene, Fluoranthene, Pyrene, Chrysene and Benzo(g,h,i)perylene, all the other PAHs were not detected in the control samples. Naphthalene recorded highest value in Opolo which was followed by Tombia, Igbogene and Swale. Rumuokoro and the control recorded zero Naphthalene. 2-Methyl Naphthalene was only reported in Opolo and Tombia. Acenaphthylene was highest in Opolo, followed by Tombia and not detected at all in Rumuokoro samples. Fluorene, Phenanthrene and Anthracene had higher concentration values in Opolo more than other sampling locations. Fluoranthene, Chrysene, Benzo(k)fluoranthene, Dibenz(a,h)anthracene were more in Rumuokoro abattoir. Benzo(b)fluoranthene and Indeno(1,2,3,c,d)pyrene were found to be highest in Igbogene. Benzo(a)pyrene and Benzo(g,h,i)perylene were highest in Tombia. The abattoir located in Opolo recorded the highest concentration of Total PAHs which was followed by Tombia, Rumuokoro, Igbogene, and Swale. The least concentration of total PAHs was observed in the control. The decreasing order of mean concentration of total PAHs in wastewater samples is as: Opolo > Tombia > Rumuokoro > Igbogene > Swale > Control. The results obtained in this study imply that polycyclic aromatic hydrocarbons are in high concentrations in most abattoirs in the study areas. Both Acenaphthene and Acenaphthylene recorded relatively high concentrations in Opolo and Tombia abattoirs. While other abattoirs recorded relatively lower concentrations. These two PAHs are noted to be readily degraded by photooxidation. Consequently, the duration of time from their deposition and the time the sample was picked and analyzed may not have given room to the degradation of these PAHs by photooxidation. The two abattoirs with high concentration values of Acenaphthene and Acenaphthylene (and also highest values of total PAHs) are abattoirs that make use of confined containers for washing abattoirs products thus giving room to accumulation of PAHs as the day progresses. Swale abattoirs where the washing of abattoir products were carried out in a flowing water body recorded the least values of Acenaphthene and Acenaphthylene and also least total PAHs value. According to Macnaughton *et al.*, (1999) the presence of hydrocarbons in an environment selects for microorganisms capable of surviving toxic contamination which concomitantly may result to the degradation of such hydrocarbons. Consequently, the presence of hydrocarbons may have resulted in the enrichment of hydrocarbon utilizers in an

hydrocarbon polluted environment. The United States Environmental Protection Agency (US EPA) has classified seven PAH compounds as being potentially carcinogenic including benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene, and indeno[1,2,3-cd]pyrene. Some of the carcinogenic PAHs were detected in the abattoir location studied. The PAHs constituents in the wastewater do find their way into the receiving water bodies and thereby impacting them. Inasmuch as these wastewaters are discharged indiscriminately into adjoining rivers, they eventually find their way into the flora and fauna of the river and/or are imparted directly on humans who depend on the river water for domestic and other uses. As these wastewaters from the slaughter and dressing grounds in the abattoir are washed into open rivers untreated for instance, Odeyemi (1991) observed that untreated wastes generated at the zoo park slaughter house in Port-Harcourt town were channeled directly into Oginigba River, one of the tributaries of the River Niger in Nigeria. This same practice was also recorded by Aniebo *et al*. (2009) who assessed indiscriminate disposal of blood wastes at the Rumueme slaughter house also in Port-Harcourt

The Heavy metals examined in the wastewater samples obtained from the abattoirs include Pb, Cd, Cr, Hg, Ni and Fe. Chromium (Cr) was detected in wastewater from all the abattoir locations. Chromium can be acquired through dermal contact or inhalation. Toxicity of Chromium is associated with allergic dermatitis in humans; arsenic is associated with skin damage, increased risk of cancer and problems with circulatory system (Scragg, 2006). Chromium is also of significant importance in altering the immune response by immunostimulatory or immunosuppressive processes (Richa *et al.,* 2002). Hexavalent chromium compounds have also been implicated in causing lung cancers in humans.

5. Conclusion and Recommendation

This study observed that abattoir wastewater obtained in the various locations contained polycyclic aromatic hydrocarbon including heavy metals such as chromium. Receiving water bodies could be impacted, especially as streams and rivers still serves as major sources of water supply in developing countries like Nigeria. The reduction of PAHs and heavy metal contamination and/or bioaccumulation in aquatic organisms, which will eventually climb through the food web to humans, can be achieved through the application of appropriate treatment processes of abattoir wastes. Summarily, there is an unapologetic need for policies to be put in place in Nigeria for the treatment of abattoir wastes before discharging them into rivers because of the public health risks and hazards associated with human exposure to PAHs and heavy metals.

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