Oral Bioaccessibility of Polycyclic Aromatic Hydrocarbons in Fly Ash Derived from Incineration of Petroleum Products and Wasted Motor Tyres in Rivers State, Nigeria

ABSTRACT

Aim: The aim of this study is to generate and investigate oral bioaccessibility based on the health risk of polycyclic aromatic hydrocarbon (PAHs) in fly ash from waste tyres and petroleum products in Rivers State, Nigeria.

Study Design: Crude oil, crude oil asphalt, artisanal diesel, refined diesel, waste engine oil and waste tyres samples were collected and incinerated. The different fly ash sampleswere analyzed with GC-MS

Place and Duration of Study: Rivers State is a state that is rich in oil in the Niger Delta area of Nigeria. The State has been experiencingthe release of soot into the environment for more than five (5) years now. This soot is noticeable to all residents of Port Harcourt and its environment with soot covering both indoor and outdoor objects such as clothes, cars, houses, floors, soil, water body, etc. The five (5) petroleum products and waste tyres samples were collected and incinerated for six (6) weeks(22nd of June to 7th of August 2021).

Methodology: The petroleum products and waste tyres samples were collected and incinerated. The different fly ash samples were collected after combustion daily. The total and oral bioaccessible PAH concentrations were determined using GC-MS. The oral bioaccessibility of PAHs in the fly ash was evaluated usingthe physiologically-based extraction test method (PBET) to determine the bioaccessible concentrations of 16 priority US Environmental Protection Agency (USEPA) PAHs in fly ash samples. The results obtained for PAHs were used for health risk assessment.

Results:A wider range of total PAH concentrations were observed in the six (6) fly ash samples from 49.71 to 926.62 mg/kg. The PAHs concentrations were significantly higher in higher molecular weight PAHs (with benzene of 4-5-6 rings) than lower molecular weight PAHs (benzene of 2-3 rings). Naphthalene, acenaphthylene, acenaphthene, and fluorene with 2-3 ring structures had the highest bioaccessible concentrations in both gastric and gastrointestinal phases of all the six fly ash samples studied.Flourene had the maximum percentage bioaccessibility of 91.30 % in the gastric phase from locally refined diesel fly ash whilst acenaphthene had maximum percentage bioaccessibility of 98.75% in the gastrointestinal phase from crude oil asphalt fly ash.

Conclusion: Data obtained from this study indicated that crude oil fly ash is a potential point source of toxicpolycyclic aromatic hydrocarbons with significant levels of health risk to humans.

Keywords:Fly ash; Oral bioaccessibility; Incineration;Physiologically based extraction test;Polycyclicaromatic hydrocarbons.

1 INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are distributed widely in our environment. Human activities which include the burning of fossil fuel, refining of petroleum, oil spill, and open incineration of waste among others lead to a substantial amount of PAH concentration in our environment. PAHs have been listed by the United States Environmental Protection Agency (USEPA) and the European community as priority pollutants" [1]. PAHs are characterized by low aqueous solubility, low vapour, and hydrophilic properties that stay long in both soils and dust. The effect of these pollutants on human health makes it necessary to determine exposure to humans from environmental matrices like soil, dust and even food" [2]. Human exposure to PAHs occurs majorly from three pathways: inhalation, dermal and ingestion, but oral ingestion has been recognized as the major exposure route for humans to soils and dust contaminants, most especially for children as a result of hand-to-mouth activities. These environmental contaminants are now common in our surroundings via incessant oil spills from auto-mechanic workshops and artisanal mining refining" [3]. Direct contact between polluted soils or dust and people represents a risk to human health. Street dust may be very harmful to humans and dust particles can also become airborne as a result of vehicular traffic and other anthropogenic activities" [4 – 6]. This may enter into the human body through the respiratory tract. In order to ascertain the potential health effect as a result of PAHs in the environment, total recoverable concentrations are studied alongside different environmental matrices, in-vitro bioaccessibility, particle size, dose-response effect and exposure pathways"[1]. Bioavailability and bioaccessibility will be discussed in this study in terms of people ingesting contaminated fly ash. The oralbioavailability of a substance may be defined as the fraction of an administered dose that enters into the bloodstream compartment from the gastrointestinal tract" [7]. Oral bioaccessibility can also be defined as the contaminant fraction of intake that is soluble in the human gastrointestinal system which is ready for absorption into the bloodstream" [7]. Animal-based in vitro methods have been used to determine contaminant bioavailability in soils however, due to ethical issues, differences between human and animal absorption systems and cost, limit this method" [8]. In vitro,tests may overcome some of these limitations. The methodologies to be used in this study for the estimation of the bioaccessibility of PAHs arein vitro physiologically based extraction methods.

The Physiologically Based Extraction Test (PBET) a standardized in vitro bioaccessibility test for organic and inorganic pollutants was developed by members of Bioaccessibility Research Group Europe (BARGE)" [9]. Understanding of the bioaccessibility/bioavailability of pollutants is essential for risk base assessments most importantly in risk base clean-up when a level of remediation is to be decided" [10].

The use of artisanal refineries for the production of some petroleum products has been the major source of fly ash in Rivers State and its environment. In the past few years, emissions from artisanal refineries have been a major concern among the residents of Port Harcourt in Rivers State, Nigeria" [11]. According to sources, it was first observed in November 2016 by Allen [12] and is known to have adverse health effects on humans and the global environment. Fly ash particles which are mainly 10 – 300nm in diameter can be absorbed into the lungs, leading to respiratory diseases such as bronchitis and asthma. The particles which are small enough to pass into the bloodstream can cause possible heart diseases" [13]. However, incomplete combustion of petroleum and its products releases unwanted pollutants into the atmosphere (such as soot, fly ash, CO, uncombusted Fuel etc.), and this has its own climate and air quality impact. Bond et al. [14] suggested that the carbonaceous component of soot is the second most vital pollutant emission after CO_2 which makes it closely related to global warming; it is also a stronger absorber of solar energy. Polycyclic Aromatic Hydrocarbons (PAHs), which are one of the compounds that form soot has been classified to be a carcinogen by the International Agency for Research on Cancer (IARC). Hence, there is a need for an assessment of bioaccessibility based on the health risk of PAHs in fly ash samples. This initial information will be useful to the Nigeriangovernment to prioritize monitoring and tracking of point sources generating petroleum base fly ash.

2. Material and methods

2.1 Study site

Crude oil, artisanal diesel and crude oil asphalt were sourced from the exclusive area of Bile Town in an artisanal refinery site in Degema Local Government Area, Rivers State. The refined diesel was bought from Nigeria National Petroleum Corporation (NNPC) Filling Station Omachi Junction Rumuodomaya while waste oil from the vehicle was collected from AY Automobile Workshop site at Obiripere Bridge Rumuosi all in Obio/Akpo Local Government Area of Rivers

State. The waste tyerswere collected from Mr AdeOjo'svulcanizer shop at Peter OdiliRoad Port-Harcourt Local Government Area of Rivers State (Figure 1).

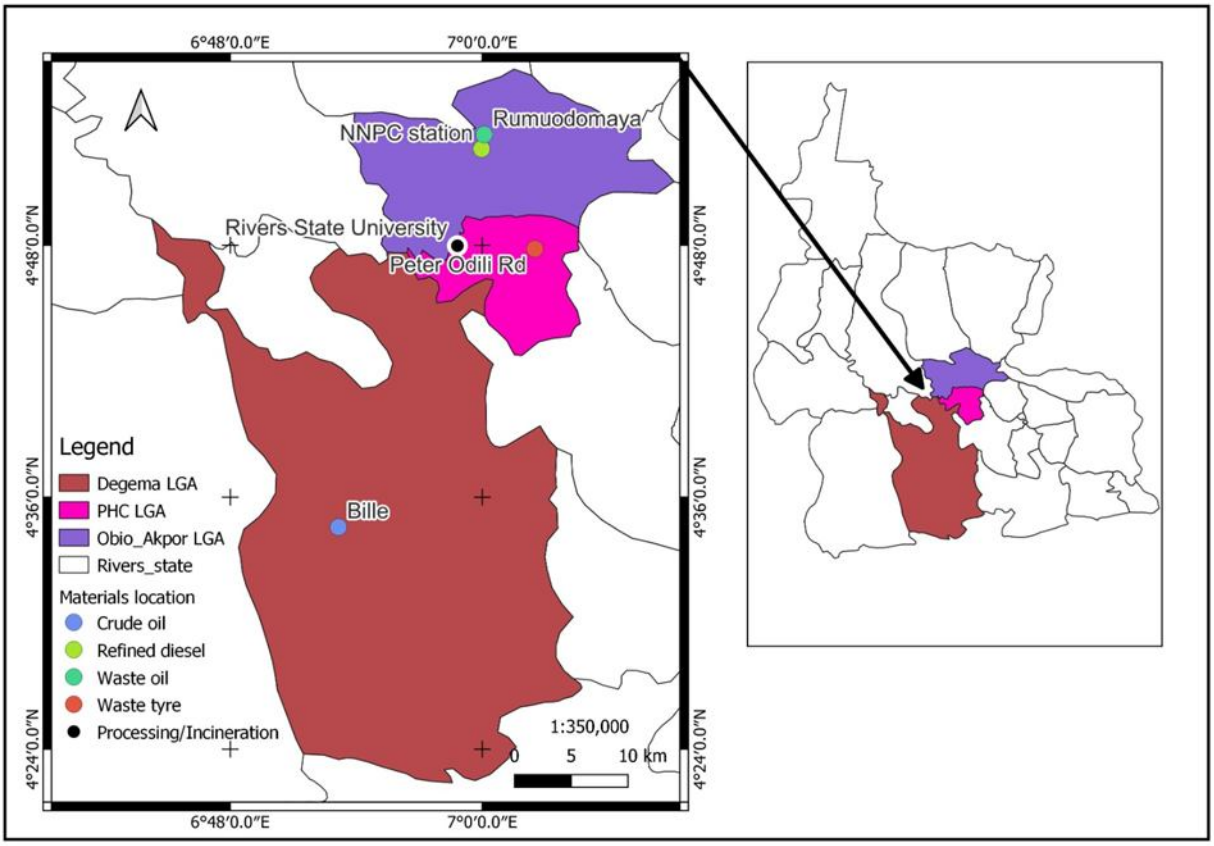

Fig. 1 Locational Map of Sources of Materials in Rivers State

2.2 Sample collection, preparation and incineration

The Crude oil, artisanal diesel, crude oil asphalt, refined diesel and waste oil were all collected with well-labelledgallons. About 10 litresvolume of each of thesampleswere transported to the Department of Chemistry Research Laboratory, Rivers State University, Port-Harcourt Nigeria, where the samples were been kept. The waste tyres were cut into smaller pieces with the well-sharpened new knife for easy combustion and it was also preserved with other samples before incineration. About 75cl of each of the crude oil and its products and 1kg of the waste tyres were introduced into the aluminium pot inside the combustion compartment and then ignited with the help of a lighter. Usually fly ash samples were passed through the flue gases for the period of incineration to the chimney and settled into the white tiles on the ashtray whilst some escaped into the environment and the bottom ash was deposited in the aluminium pots.

2.3 Sampling of fly ash

To acquire descriptive samples and generate an adequate quantity of fly ash for laboratory analysis, each material was incinerated for four days and samples were collected instantly after combustion daily. After the burning of each material, fly ash was deposited on the white tiles on the ashtray under the hood and on the inner wall ofthe chimney, frustum and hood of the incinerator. The deposited fly ash on the white tiles was harvested onto a clean 250ml Pyrex conical flask with the aid of a brush and then transferred into amber bottles and firmly corked. The samples were then transferred to the Department of Chemistry Post Graduate Laboratory Rivers State University, Port-Harcourt Nigeria and stored in a very cool dry box at room temperature.

2.4 Extraction procedures

2.4.1 Extraction and clean-up of PAHs in fly ash

The ultrasonic extraction process was used during this study. 0.3g of fly ash was weighed into a clean labelled beaker and 30 ml of 1:1 mixture of Dichloromethane (DCM) and Acetone were added to the fly ash sample. The samples were extracted ultrasonically using a sonicator (Bransonic Ultrasonic Cleaner 2200) to agitatefor 1 hour with intervals of 15 minutes and allowed to settle for 10 minutes. The extraction was carried out in triplicate per each of the samples. The extracts were decanted into clean well-labelled beakers and the combined extract was spiked with internal standard solution O-terphenyl and each sample was concentrated to 1ml under nitrogen in a fume cupboard.

Cartridges were used for the clean-up of the extract, the cartridges were pre-conditioned using glass wool, 10g of activated silica gel and 5g of activated anhydrous sodium sulphate (Na_2SO_4) to remove any traces of water in the extract. I then formed a slurry using DCM for aromatic (PAHs) samples. The 1 ml concentrated extract was loaded on each pre-conditioned cartridge and eluted with DCM for PAH samples. Eluates were concentrated in a fume cupboard naturally to 1ml and normal anhydrous $Na_2SO_4$was added into each sample before being decanted into vials and then preserved in the refrigerator at 4^oC before the analysis.

2.4.2 Oral bioaccessibility or in-vitro gastrointestinal extraction

A precisely 0.3g of fly ash sample was weighed out into three different properly labelled (50mL) screw cap Sarstedttubes in triplicate each for the gastric phase and gastrointestinal phase. 4.5 mL of simulated saliva fluid was added manually shaking the mixture in the screw-cap vessel. Subsequently, after 15 minutes 6.75 mL of simulated gastric fluid was added. The mixture was then capped and placed on an end-over-end shaker maintained at 37 ± 2 °C for 1 hour. Then, the pH of the fly ash suspensions was observed; the pH needed to be within the range (1.2-1.7) and the tubes were centrifuged at 3000rpm for 5-10 minutes and the aliquot of supernatant were removed and 0.1ml HNO_3 and the extract were kept at $<4^oC$ before the analysis

The procedure of extraction above was applied for the gastrointestinal phase, moreover, 13.5ml of simulated duodenal fluid and 4.5ml of simulated bile were added by manually shaking the mixture in the screw-cap vessel after the initial 1-hour extraction at 37^oC. The mixture's pH was adjusted to 6.3 ± 0.5, by the dropwise addition of 37 % HCI v:v, 10 M NaOH, as required. The mixtures were then placed on an end-over-end shaker at 37^oC (human body temperature) for another 4 hours inside the ovum. The solutions were later centrifuged at 3000g for 10 minutes and the aliquot of the supernatant was taken. All the in vitro analyses were done in triplicates for each sample.

At the end of the process, the liquid phase both gastric and gastrointestinal solutions decanted (19.5ml) were extracted with a 40 ml mixture of DCM and acetone (1:1) for 10 minutes and the process was repeated three times with the aid of a separatory funnel while reducing the solvent volume by 50% each time. Sodium sulfate was added to the combined extract to remove any water content that might be present in the extract. The solvents were concentrated in 1 ml. The extracts were later cleaned with pre-conditioned cartridges using glass wool, 10g of activated silica gel and 5g of activated anhydrous sodium sulphate (Na_2SO_4) to remove any traces of water from the extracts. The slurry was formed with n-hexane and 1 ml concentrated extract was loaded on each pre-conditioned cartridge and eluted with DCM. Afterwards, the eluted fraction was again concentrated in a fume cupboard naturally to 1ml and normal anhydrous Na_2SO_4 was added into each sample before being decanted into vials and then preserved in the refrigerator at 4^oC before PAHs analysis. The final concentrated extract was then analyzed using GC-Agilent Technologies 7890A coupled with a Mass Spectrometry (Agilent 5975C VL MSD with Triple-axis Detector) and an Agilent Technologies 7693 autosampler injector, as described below.

2.4.3 Instrumentation and Analysis

In an effort to acquire the total PAH concentration in the fly ash following the simulated in vitro gastrointestinal tests, the analytical method used was GC-MS aimed at the analysis of PAHs in fly ash. The distinct GC-MS systems were used, Unified BARGE Method (ion trap). Employing a quadrupole rather than an ion trap will decrease instrument sensitivity and increase robustness. The GC-MS instrument, employed to analyze the extract from the UBM and total PAHs, was a GC-Agilent Technologies7890Aconnected with a splitless injector with a HP-5MS UI capillary column (30 m long, 250 µmi.d ×0.25 µm film thickness) coupled with a mass spectrophotometer detector (Agilent 5975C VL MSD with Triple-axis Detector) and an Agilent Technologies 7693auto sampler injector was used for the quantification of PAHs from the samples. A five-point calibration curve was adopted for quantification on the GC-MS. The samples were injected (1 µL) in the splitless mode, with the front inlet temperature of 250 ^{o}C the initial oven temperature of 100^{o}C and a final temperature of 320 ^{o}C. The carrier gas used was helium with a flow rate of (1.5 mL/min). Electron ionization at 70 eV was used to detect mass spectra. PAHs identification was a result of the validation of retention time and abundance of quantification ions compared with the standard. Selective ion monitoring (SIM) modes were used to quantify individual PAH compounds. GC-MS Chemstation software was used to collect chromatographic data. The detection limit for all 16 PAHs was 0.001-0.01 mg/L.

3. Results and discussion

3.1 Total PAHs Concentrations in Fly Ash

The concentrations of total PAH in six (6) fly ash samples are provided in (Figure 2). A wider range of total PAH was observed in fly ash samples from 49.71 to 926.62 mg/kg. These values are highercompared to the values of total PAH reported by Kati*et al*. [15] and Aryal*et al*. [16] (1.6 – 25.30 mg/kg). The total PAH concentrations from CAF and COF fly ash were significantly higher than those of WTF, WOF, LDF and RDF fly ash. Generally, the results of total PAHs concentrations trend are crude asphalt fly ash (926.62 mg/kg), crude oil fly ash (738.28 mg/kg), waste tyres fly ash (333.69 mg/kg), waste oil fly ash (330.11 mg/kg), locally refined diesel fly ash (119.92 mg/kg) and refined diesel fly ash (49.71 mg/kg). The results from this study indicated that the fly ash samples studied had total PAH concentrations above the generally accepted threshold for total PAHs of 40 mg/kg [17].

3.2 Total Concentrations of Individual PAH in the Fly Ash Samples

The concentrations of each individual PAH in fly ash samples are shown in (Figure 3). The concentrations of PAHs with five and six rings high molecular weight PAHs that is dibenzo{a,h}anthrancene, indenol{1,2,3-cd}pyrene, benzo{ghi}pyrene, benzo{k}fluoranthene and benzo{b}fuoranthene were relatively high except benzo{a}pyrene. The concentrations of PAHs with low molecular weight i.e. naphthalene, acenaphthene, acenaphthene, fluorene, phenanthrene and anthracene with 2-3 rings structures were very low but higher than the values reported by (Valerie*et al.*, 2021) in all the fly ash samples analysed. That of moderate molecular weight PAHs with 4 rings structure i.e. fluoranthene, pyrene, benzo {a}pyrene and chrysene were also high but not as that of PAHs with five and six rings structures. Generally, concentrations of dibenzo{a,h}anthrancene in this study recorded the highest values among the 16 PAH compounds, refined diesel fly ash recorded the least mean values of 4.69 ± 0.04 mg/kg while crude asphalt fly ash recorded the highest mean values of 154.43 ± 7.54 mg/kg Figure 4.2b. Acenaphtylene concentrations recorded the least values in the fly ash samples study ranging from refined diesel fly ash mean value (0.27 ± 0.04 mg/kg) to that of crude oil fly ash with a mean value (1.25 ± 0.33 mg/kg). The individual PAHs distributions in crude asphalt fly ash indicated a higher concentration in all the 16 PAHs compound from this study except that of naphthalene, acenaphthene, acenaphthene, and fluorine which is lower compared with that of crude oil fly ash. All the compounds have a median below 40 mg/kg except indenol{1,2,3-cd}pyrene, benzo{ghi}pyrene and dibenzo{a,h}anthrancene that is above 40 mg/kg concentrations. This study also indicated that all the compounds have mean values below 40 mg/kg except indenol{1,2,3-cd}pyrene, benzo{ghi}pyrene,dibenzo{a,h}anthranceneand benzo{b}fuoranthenethat shown mean values above 40 mg/kg concentrations.

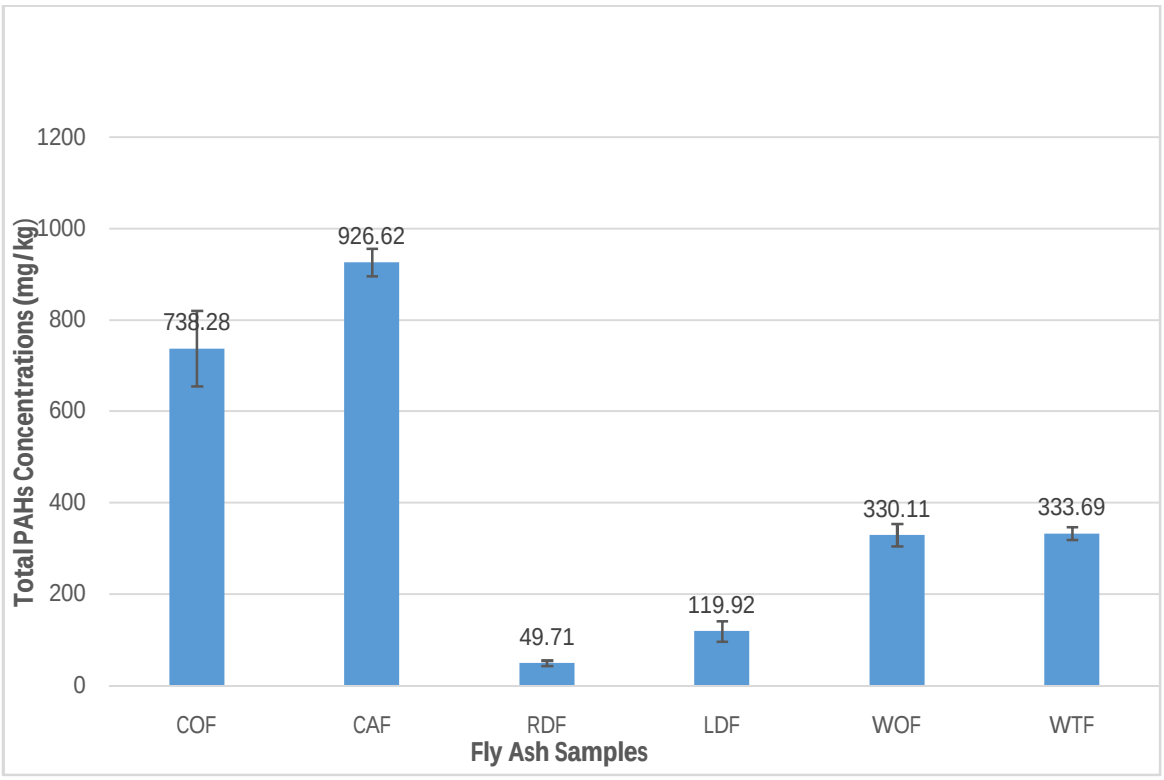

Fig 2. Error Bar of Total PAHs Concentrations in Fly Ash Samples

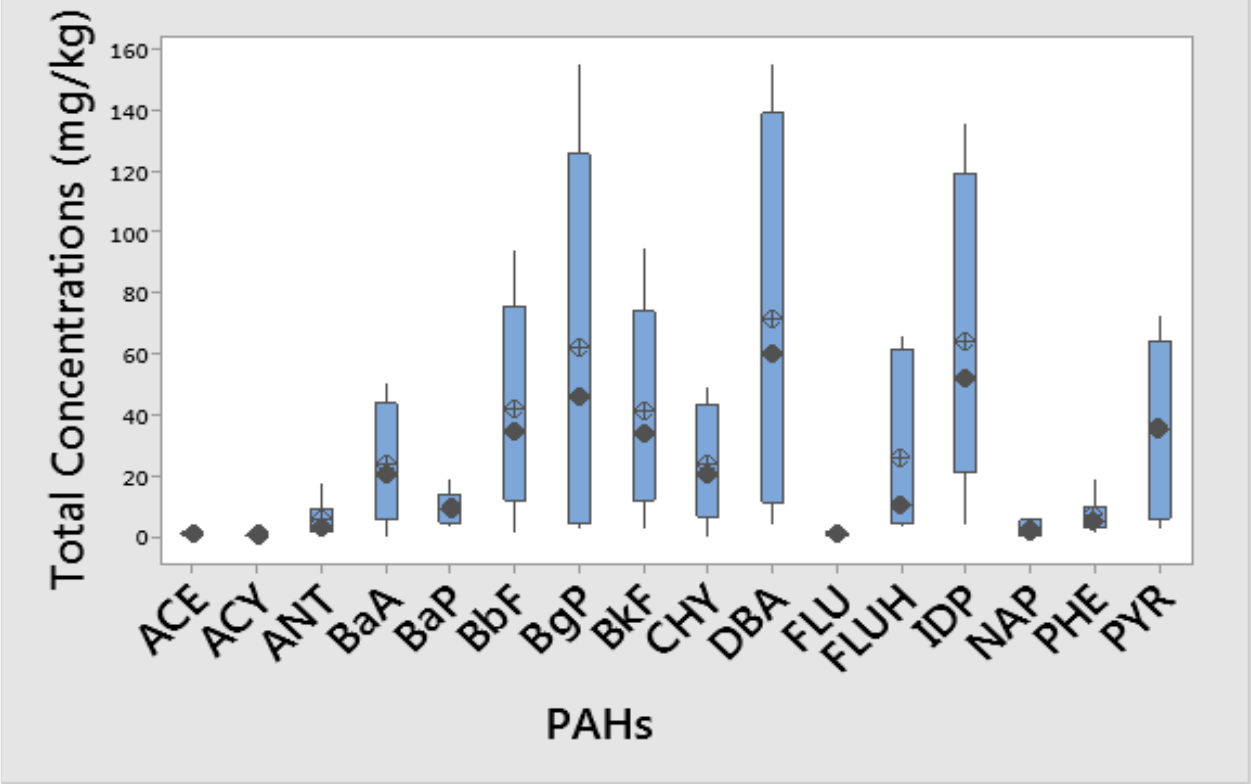

Fig. 3. BoxplotBoxplot of individual PAH concentrations in Fly Ash samples.

Naphthalene (Nap), Acenaphthylene (ACY), Acenaphthalene (ACE), Fluorene (FLU), Phenanthrene (PHE), Anthracene (ANT), Fluoranthene (FLUH), Pyrene (PYR), Benzo(a)anthracene (BaA), Chrysene (CHY), Benxo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Indeno(1,2,3-cd)pyrene (IDP), Dibenzo(a,h)anthracene (DBA), Benzo(g,h,i)perylene (BgP)

3.3 Bioaccessible Concentrations of PAHs in Fly Ash Samples

The bioaccessible portions for the 16 PAHs, found with the aid of the Unified Berge Method were calculated using total fly ash concentrations and concentrations gotten after the PBET extraction.The bioaccessible concentrations of total PAHs in all six (6) fly ash samplesfrom this studyare provided in (Table 1).The % bioaccessibility of total PAHs in all six (6) fly ash samples (COF, CAF, RDF, LDF, WOF and WTF)from this studyare providedin (Table 1). The maximum % bioaccessibility fractions in RDF with the value of 46.35 % while the minimum values of 12.48 % in COF were observed in this study. Generally, PAH % bioaccessibility from COF,

CAF, RDF and WTF were significantly more bioaccessible in the gastrointestinal phase except for LDF and WOF which is more bioaccessible in the gastric phase. Considering the % bioaccessibility of fly ash in this study CAF happened to have the highest risk to human health because of the PAHs % bioaccessibility (23.22 %) to the total PAHs concentrations of (926.62 mg/kg) followed by COF with % bioaccessibility of (12.48 %) to its total PAHs concentrations of (738.28 mg/kg). Total PAHs % bioaccessibility for the fly ash that ranged from 12.48 % to 46.35 % is similar to those one reported by Min NL*et al*. [18] that reported % bioaccessibility ranged from 14.6 % to 63.2 % in the gastrointestinal phase of topsoil from different urban functional areas and Sardar*et al*. [19] who reported % bioaccessibility ranged of 27.4 % to 52.8 % in the gastrointestinal phase respectively. In crude oil fly ash (COF) analyzed in this study showed that FLU has the highest % bioaccessibility of 76.43 % in the gastric phase and 58.60 % of FLU in the gastrointestinal phase against the BgP that has the least % bioaccessibility of 0.72 % in gastric phase and 0.80 % of FLUH in gastrointestinal phase in all the 16 PAHs studied. Similarly, in crude oil asphalt fly ash CAF analyzed FLU has the highest % bioaccessibility 80.65 % in the gastric phase and 98.75 of ACE in the gastrointestinal phase against the lowest % bioaccessibility of 0.53 % of PHE and 1.58 % of IDP in gastric and gastrointestinal phases respectively. The % bioaccessibility of refined diesel fly ash RDF in this study was observed to have the highest bioaccessibility fraction of 87.65 % of BbF in the gastric phase and 98.75 % of ACE in the gastrointestinal phase, which is the most % bioaccessibility in all the 16 PAHs analyzed among the six fly ash samples studied except unusual high ACY .percentage bioaccessibility that is above 100%. However, the lowest bioaccessible fraction in both gastric and gastrointestinal phases were 6.00 % of ANT and 3.22 % of ANT respectively. Locally refined diesel fly ash observed was not detected in NAP in both gastric and intestinal phases with the highest % bioaccessible of 103 57 % ACY and 64.29 % ACY in gastric and intestinal phases respectively. The highest % bioaccessibility was observed in waste oil fly ash WOF with a value of 33.70 % of ACE in the gastric phase and 80.95 % ACY whereas, no value was detected in the gastric phase and the least value of 0.34 % of BaP in the gastrointestinal phase.

Finally, waste tyres fly ash WTF in this study indicated FLUH with the highest value of 54.86 % in the gastric phase and 69.23 % ACY in the gastrointestinal phase respectively with the lowest values recorded in ACY BgP 2.77 % in the gastric phase and 5.90 % BaP in gastrointestinal

phase. Generally, unexpected high bioaccessibility for acenaphthene in almost all the fly ash samples analyzed in both phases compare with other PAHs from this study.

Table1: Total PAH Content, Gastrointestinal Digest Fractions and Total Bioaccessible Fraction for the 16 PAHs in Fly Ash Samples

Fly Ash Samples	Total PAHs Content (mg/kg)	Gastrointestinal Digest (mg/kg)	BAF (%)
COF	738.28	32.71	12.48
CAF	926.62	46.34	23.22
RDF	49.71	19.53	46.35
LDF	119.92	19.42	29.88
WOF	330.11	15.65	19.05
WTF	333.69	40.58	27.74

Where COF = Crude Oil Fly Ash, CAF = Crude Oil Asphalt Fly Ash, RDF = Refined Diesel Fly Ash, LDF = Locally Refined Diesel Fly Ash, WOF = Waste Oil Fly Ash, WTF = Waste Tyres Fly Ash, BAF = Bioaccessibility Fractions

The boxplot of the individual PAHs bioaccessible concentrations from the fly ash samplesindicated indeno [1, 2, 3-c, d] pyrene has the maximum bioaccessible fractions in gastric phase ranging from (1.96 mg/kg – 8.66 mg/kg) whilst acenaphythene indicated lowest bioaccessible fractions ranging from 0.08 mg/kg – 0.16 mg/kg. However, the boxplot of the individual PAHs bioaccessible concentrations from the fly ash samples indicated benzo[b]fluorathene has the maximum bioaccessible fractions in the gastrointestinal phase ranging from (0.39 mg/kg – 15.82 mg/kg) whilst acenaphythene indicated the lowest bioaccessible fractions ranging from (0.16 mg/kg – 0.63 mg/kg).The % bioaccessibility of each individual PAH in fly ash samples shown in (Figure 4 and Figure 5) indicated that the % bioaccessibility of NAP, ACY, ACE and FLU with 2-3 rings structures were relatively high in

both gastric and gastrointestinal phases except PHE and ANT however, the higher molecular weight with 4-6 ring structure was relatively low, the decrease in bioaccessibility of individual PAHs with an increase in the ring number in both gastric andgastrointestinal phase which is similar to the result obtained by Sardar*et al*. [19] using the in vitro method, maybe due to decrease in solubility in waterand increase in K_{ow} of individual PAHs with an increase in a number of their benzene ring. Fluorene was the most bioaccessible in the gastric phase among all the sixteen PAHs studied in this research which might be a result that fluorene is highly soluble in water compare with other higher molecular weight PAHs.The same trend of results was reported by Lorenzi*et al*. [1]. Acenapthylene was observed to have the highest % bioaccessibility in the gastrointestinal phase compared to other PAHs analyzed.

The boxplot of the individual PAHs % bioaccessibility from the fly ash samples in the gastric phase (Figure 4) indicated acenaphythene with the highest upper quarter with a percentage bioaccessibility of about 103 % in the gastric phase. Also, some of the maximum upper quartiles of the bioaccessible portion showed for acenaphythene, fluorene, naphthalene, anthraceneenzo(a)pyrene, and benzo(b)fluoranthene between 60 % and 80 %. Dibenzo (a,h) anthracene, fluoranthene and phenanthrene were showing upper quartiles between 43% and 58%. The lowest maximum upper quartiles were benzo (k) fluoranthene, benzo (a) anthracene, benzo (g,h,i) prylenechrysene, indeno (1,2,3,c,d) pyrene and pyrene between 30 % and 42 %. However, none of the studied fly ash samples were in the lower quarter range. Comparing the individual PAHs concentrations with the bioaccessible fractions indicated that acenaphthalene, acenaphthylene, fluorene, naphthalene, phenanthrene, benzo(a)pyrene and anthracene with the lowest total PAH concentrations in the gastric phase appeared to be the highest bioaccessibility, as discussed above. Similarly, comparing the individual PAHs bioaccessible fractions with the % bioaccessibility fractions indicated that acenaphthalene, acenaphthylene and anthracene with the lowest bioaccessible fractions in the gastric phase happened to have the highest % bioaccessibility values, as discussed before. All the compounds analyzed in this study indicated a median and mean below 40 % except that of fluorenewhich is above 40 % in the gastric phase with a median double the concentrations range.

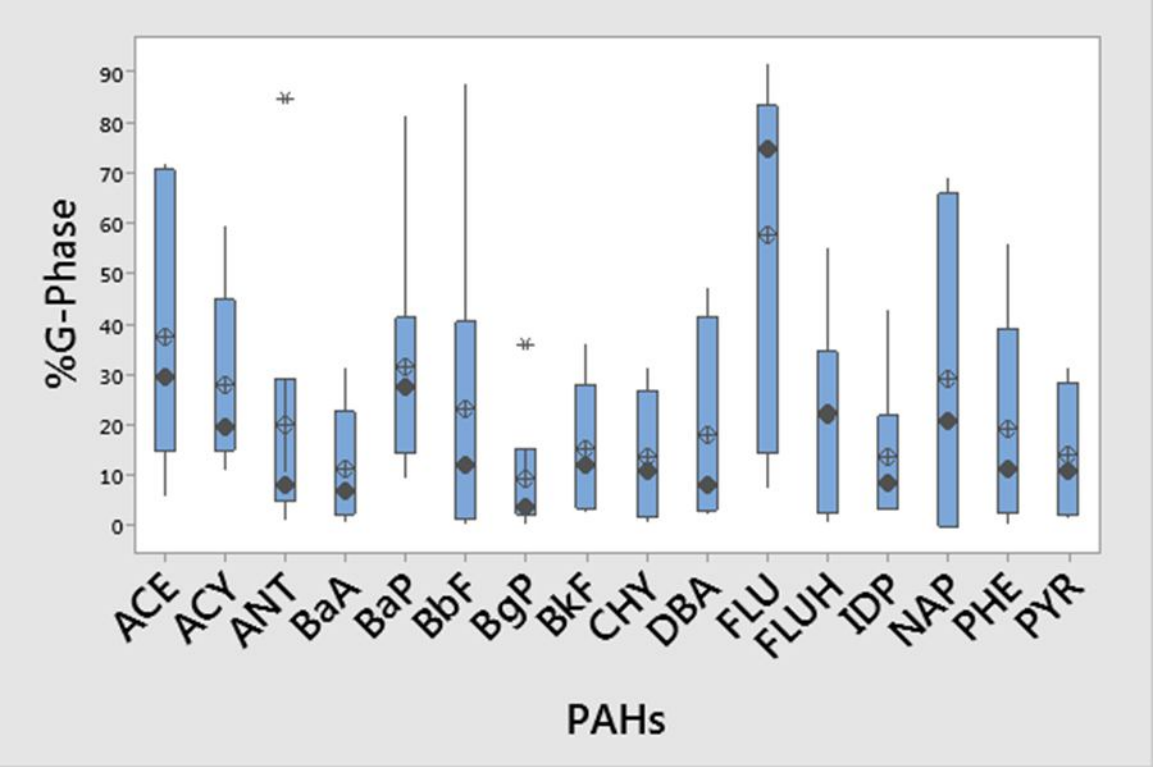

Fig. 5. Boxplot of individual PAH % Bioaccessibility in Gastric Phase from Fly Ash Samples. Gastric phase (G), Naphthalene (Nap), Acenaphthylene (ACY), Acenaphthalene (ACE), Fluorene (FLU), Phenanthrene (PHE), Anthracene (ANT), Fluoranthene (FLUH), Pyrene (PYR), Benzo(a)anthracene (BaA), Chrysene (CHY), Benxo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Indeno(1,2,3-cd)pyrene (IDP), Dibenzo(a,h)anthracene (DBA), Benzo(g,h,i)perylene (BgP)

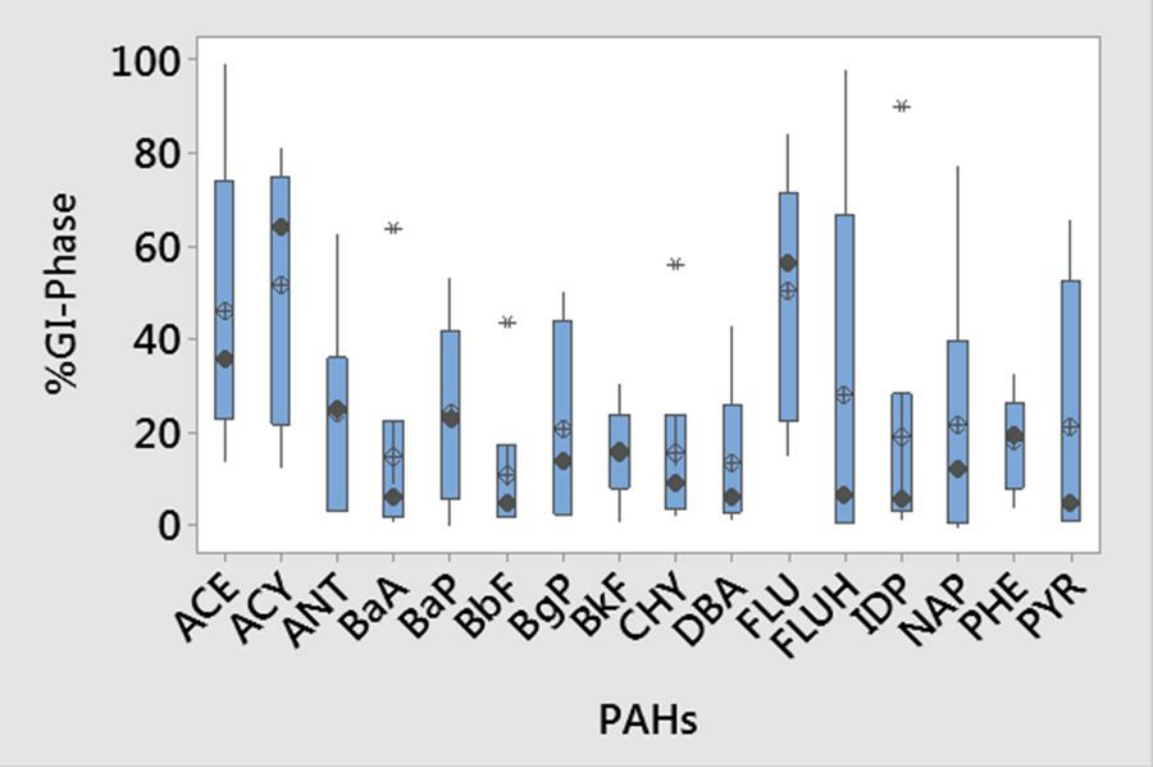

Fig 6. Boxplot of individual PAH % Bioaccessibility in Gastrointestinal Phase from Fly Ash Samples.

Gastrointestinal phase (GI),Naphthalene (Nap), Acenaphthylene (ACY), Acenaphthalene (ACE), Fluorene (FLU), Phenanthrene (PHE), Anthracene (ANT), Fluoranthene (FLUH), Pyrene (PYR), Benzo(a)anthracene (BaA), Chrysene (CHY), Benxo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Indeno(1,2,3-cd)pyrene (IDP), Dibenzo(a,h)anthracene (DBA), Benzo(g,h,i)perylene (BgP)

The individual PAHs % bioaccessibility from the fly ash samples in the gastrointestinal phase also indicated acenaphthalene with the highest upper quarter with a percentage bioaccessibility of about 98.75 % in the gastrointestinal phase. However, some of the maximum upper quartiles bioaccessible portion showed for acenaphthalene, fluoranthene, fluorene, naphthalene, anthracene, benzo(a)anthracene, pyrene and indeno (1,2,3,c,d) pyrene between 60% and 97 %. Dibenzo (a,h) anthracene, benzo(a)pyrene, chrysene, benzo(g,h,i)perylene and benzo(b)fluoranthene were showing upper quartiles between 42% and 58%. The lowest maximum upper quartiles were phenanthrene and benzo(k)fluoranthene between 30 % and 32 %.

However, none of the studied fly ash samples was in the lower quarter range in the gastrointestinal phase. Comparing the individual PAHs concentrations with the bioaccessible fractions indicated that acenaphthalene, acenaphthylene, fluorene, naphthalene, phenanthrene, benzo(a)pyrene and anthracene with the lowest total PAH concentrations in the gastrointestinal phase appeared to be the highest bioaccessibility, as discussed above. All the compounds have a median below 40 % except fluorene and acenaphthylene. This study also indicated that all the compounds have mean values below 40 %except acenaphthalene, acenaphthylene andfluorenewhichshowed mean values above 40 % in gastrointestinal phase.

4. Conclusion

The results from this study indicated that PAHs have been identified in the fly ash particulate at very relatively high concentrations. The total PAHs concentrations values observed from this study range for the six matrices were crude oil fly ash 738.28 mg/kg, crude oil asphalt fly ash 926.62 mg/kg, refined diesel fly ash 49.71 mg/kg, locally refined diesel fly ash 119.92 mg/kg, waste oil fly ash 330.11 mg/kg and waste tyres fly ash 333.69 mg/kg with refined diesel fly ash and crude oil asphalt fly ash indicated the lowest and highest concentrations respectively. The total PAH concentrations from this study were above the generally accepted threshold limit for total PAHs of 40 mg/kg. Knowing that some PAHs are carcinogenic and mutagenic in nature indicated very vital healtheffects from burning tyres, petroleum and its products. Naphthalene, acenaphthylene, acenaphthene, and fluorene with 2-3 ring structures had the highest bioaccessible concentrations in both phases of fly ash for all the samples studied. Flourene had the maximum percentage bioaccessibility of 91.30 % in the gastric phase while acenaphthalene had the maximum percentage bioaccessibility of 98.75 % in the gastrointestinal phase.

These findings suggest that fly ash from these productswas categorized as heavily contaminated, based on their total concentration of PAHs and bioaccessible percentages fraction of PAHs.As a result of the high bioaccessibility observed for most of the PAHs investigated government should prioritize monitoring and the tracking of point sources generating petroleum base fly ash in a bid to protect human health.Future studies should also be conducted on PAHs inhalation bioaccessibility from petroleum and its products fly ash.

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LIMITATIONS

Lack of fund and inability to get some of the chemicals on time really affected the research. Incineration of the samples were done in an enclosed conditions unlike fly ash from open burning of petroleum products.

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