Oral Bioaccessibility of Polycyclic Aromatic Hydrocarbons in Fly Ash Derived from Incineration of Petroleum Products and Wasted Motor Tyres.

ABSTRACT

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

Study Design: Five (5) petroleum products and waste tyres samples were collected and incinerated for six (6) weeks and the samples were collected instantly after combustion daily and analyzed with GC-MS

Place and Duration of Study: Rivers State is a state in Nigeria that is rich in oil in Niger delta area. The State has been experience 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 cloths, car, houses, floor, soil, water body, etc. The five (5) petroleum products and waste tyres samples were collected and incinerated for six (6) weeks (22^{nd} of June to 7^{th} of August 2021).

Methodology: Five (5) petroleum products and waste tyres samples were collected and incinerated for six (6) weeks and the samples were collected instantly after combustion daily. The total and oral bioaccessible PAHs concentrations were determined using GC-MS. The oral bioaccessibility of PAHs in the fly ash were evaluated using 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 were observed in fly ash samples from 49.71 to 926.62 mg/kg. The PAHs concentrations were significantly high in higher molecular weight PAHs, (with benzene of 4-5-6 rings) compared to lower molecular weight PAHs (benzene of 2-3 rings). Naphthalene, acenaphthylene, acenaphthene, and flourene with 2-3 rings 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 gastric phase from local refined diesel fly ash whilst acenaphthene had maximum percentage bioaccessibility of 98.75 % in gastrointestinal phase from crude oil asphalt fly ash.

Conclusion: Data obtained from this study indicated that crude oil fly ash as a potential point source of toxic polycyclic aromatic hydrocarbons with significant level of health risk to human.

Keywords: Fly ash; Oral bioaccessibility; In-vitro bioaccessibility; Incineration; Physiological based extraction test; Polycyclic aromatic hydrocarbons; Elements.

1 INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are distributed widely in our environment. Due to human activities which include burning of fossil fuel, refining of petroleum, oil spill, and open incineration of waste among others lead to substantial amount of PAHs concentration in our environment. PAHs has been listed by the United States Environmental Protection Agency and the European community as priority pollutants'' [1]. PAHs are characterized with low aqueous solubility, low vapour, hydrophilic properties stay long in both soils and dust. The effect of this pollutants on human health make 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 dusts contaminants, most especially for children as a result of hand to mouth activities. These environmental contaminants are now common in our surrounding via incessant oil spill from auto-mechanic workshop and artisanal mining refining'' [3]. Direct contact between polluted soils or dust and people represent a risk for human health. Street dust may be very harmful to human and dust particle 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 track. In order to ascertain the potential health effect as a result of PAHs in the environment, total recoverable concentrations are studied alongside with 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. Oral bioavailability of a substance may be defined as the fraction of an administered dose that enters into the blood stream 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 blood stream'' [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 system and cost, limit this method'' [8]. In vitro test may overcome some of these limitations. The methodologies to be used in this study for the estimation of bioaccessibility of PAHs is in 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 a 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 known to have adverse health effect on human 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 e.t.c), and this have 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 is one of the compounds that form soot has been classified to be carcinogen by the International Agency for Research on Cancer (IARC). Hence, there is need for assessment of bioaccessibility based on health risk of PAHs in fly ash samples. This initial information will be useful to Nigeria government to prioritize monitoring and the 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 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 vehicle were collected from AY Automobile Workshop site at Obiripere Bridge Rumuosi all in Obio/Akpo Local Government Area of Rivers State. The waste tyers was collected from Mr Ade Ojo vulcanizer shop at Peter Odili road Port-Harcourt Local Government Area of Rivers State (Figure 1).

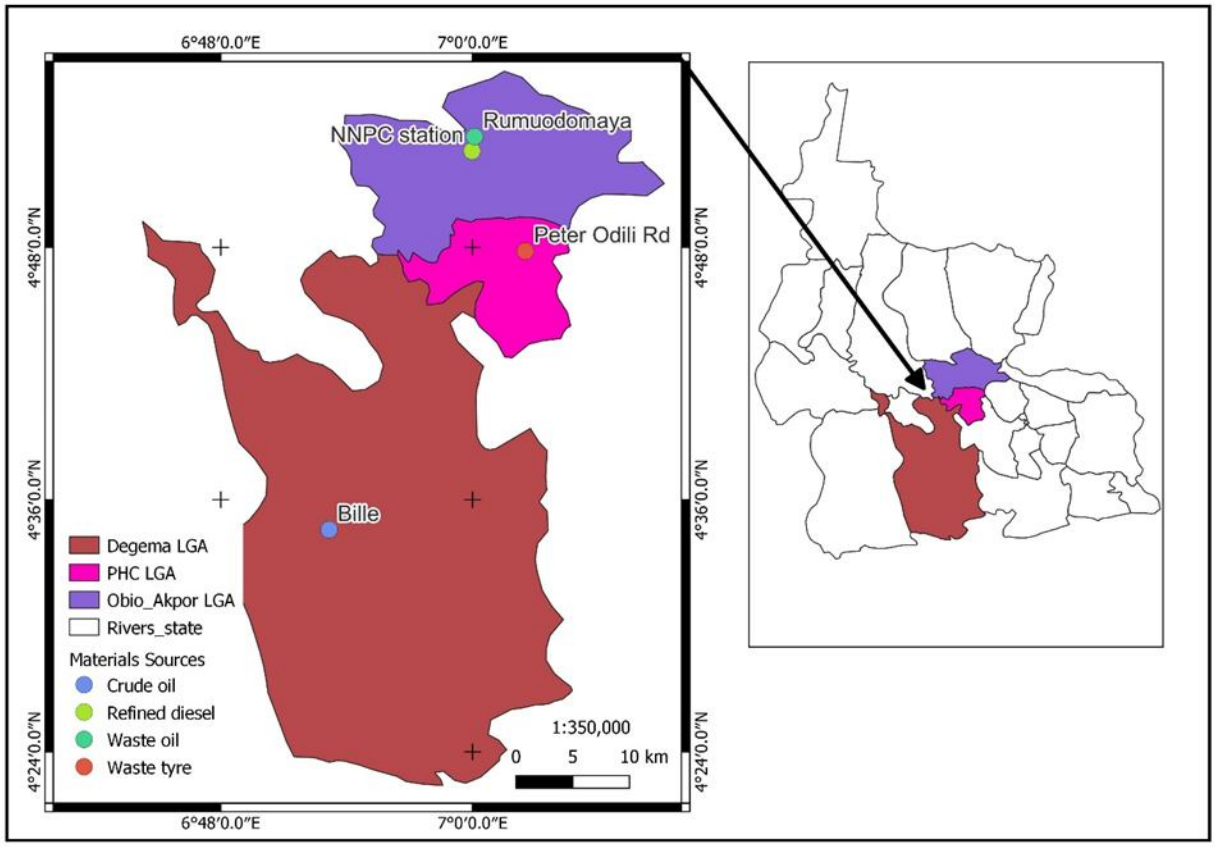

Fig. 1 Locational Map of Sources of Materials in Rivers State

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 labeled 4 liters gallon, two (2) gallons for each sample and 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 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 aluminum pot inside the combustion compartment and then ignited with the help of 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 ash tray whilst some escaped into the environment and the bottom ash were deposited in the aluminum pots.

2.3 Sampling of fly ash

To acquire descriptive samples and generate 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 ash tray under the hood and on the inner wall o chimney, frutrum and hood of incinerator. The deposited fly ash on the white tiles were harvested onto clean 250ml Pyrex conical flask with the aid of 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

Ultrasonic extraction process was used during this study. 0.3g of fly ash was weighed into a clean labelled beaker and 30ml of 1:1 mixture of Dichloromethane (DCM) and Acetone were added into the fly ash sample. The samples were extracted ultrasonically using sonicator (Bransonic Ultrasonic Cleaner 2200) to agitate 1 hour with interval 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 were 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 slurry using DCM for aromatic (PAHs) samples. The 1ml concentrated extract were loaded on each pre-conditioned cartridges and eluted with DCM for PAHs samples. Eluates were concentrated in a fume cupboard naturally to 1ml and normal anhydrous Na_2SO_4 were added into each samples before 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 Sarstedt tube in triplicate each for the gastric phase and gastrointestinal phase. 4.5 mL of simulated saliva fluid was added and manually shaken the mixture in the screw-cap vessel. Subsequently, after15 minutes 6.75 mL of simulated gastric fluid was added. The mixture was then caped 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 was 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^{o}C before the analysis

The procedure of extraction above was applied for 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^{o}C. The mixtures pH was adjusted to 6.3 ± 0.5, by the drop wise addition of 37 % HCI v:v, 10 M NaOH, as required. The mixtures were then placed on end-over-end shaker at 37^{o}C (human body temperature) for another 4 hours inside the ovum. The solutions were later centrifuged at 3000g for10 minutes and the aliquot of the supernatant were taken. All the in vitro analysis 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 40 ml mixture of DCM and acetone (1:1) for 10 minutes and the process was repeated three times with the aid of 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 to 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. Slurry was formed with n-hexane, 1ml concentrated extract were loaded on each pre-conditioned cartridges and eluted with DCM. Afterward, the eluated fraction was again concentrated in a fume cupboard naturally to 1ml and normal anhydrous Na_2SO_4 was added into each samples before decanted into vials and then preserved in the refrigerator at 4^{o}C 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 auto sampler injector, as described below.

2.4.3 Instrumentation and analysis

In an effort to acquire the total PAHs 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 splitless injector with a HP-5MS UI capillary column (30 m long, 250 µm i.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,front inlet temperature of 250 ^{o}C with the initial oven temperature of 100 ^{o}C and final temperature of 320 ^{o}C. The carrier gas used was helium with flow rate of (1.5 mL/min). Electron ionization at 70 eV was used to detect mass spectra. PAHs identification was as a result of validation of retention time and abundance of quantification ions compared with the standard. Selective ion monitoring (SIM) mode were used to quantify individual PAH compounds. GC-MS Chemstation software were used to collect chromatographic data. The detection limit for all the 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 3. A wider range of total PAH were observed in fly ash samples from 49.71 to 926.62 mg/kg. These values are higher compare to 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 is: 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), local 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 PAHs 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 shown in (Figure 2) 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. naphtalene, acenaphtylene, acenaphtene, fluorene, phennthrene 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 compound, 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. 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 the mean value (1.25 ± 0.33 mg/kg). The individual PAHs distributions in crude asphalt fly ash were indicated a higher concentration in all the 16 PAHs compound from this study except that of naphtalene, acenaphtylene, acenaphtene, and fluorine that is lower compare with that of crude oil fly ash. All the compounds have 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}anthrancene and benzo{b}fuoranthene that shown mean values above 40 mg/kg concentrations.

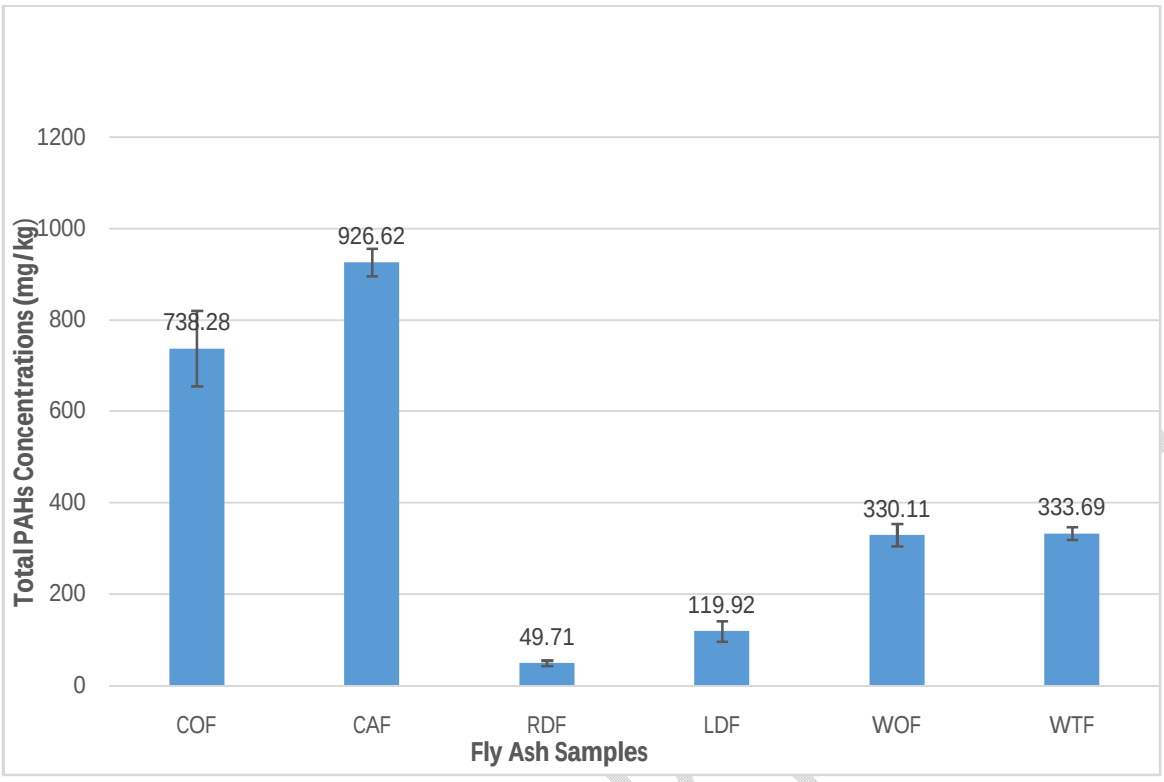

Fig 2. Error Bar of Total PAHs Concentrations in Fly Ash Samples

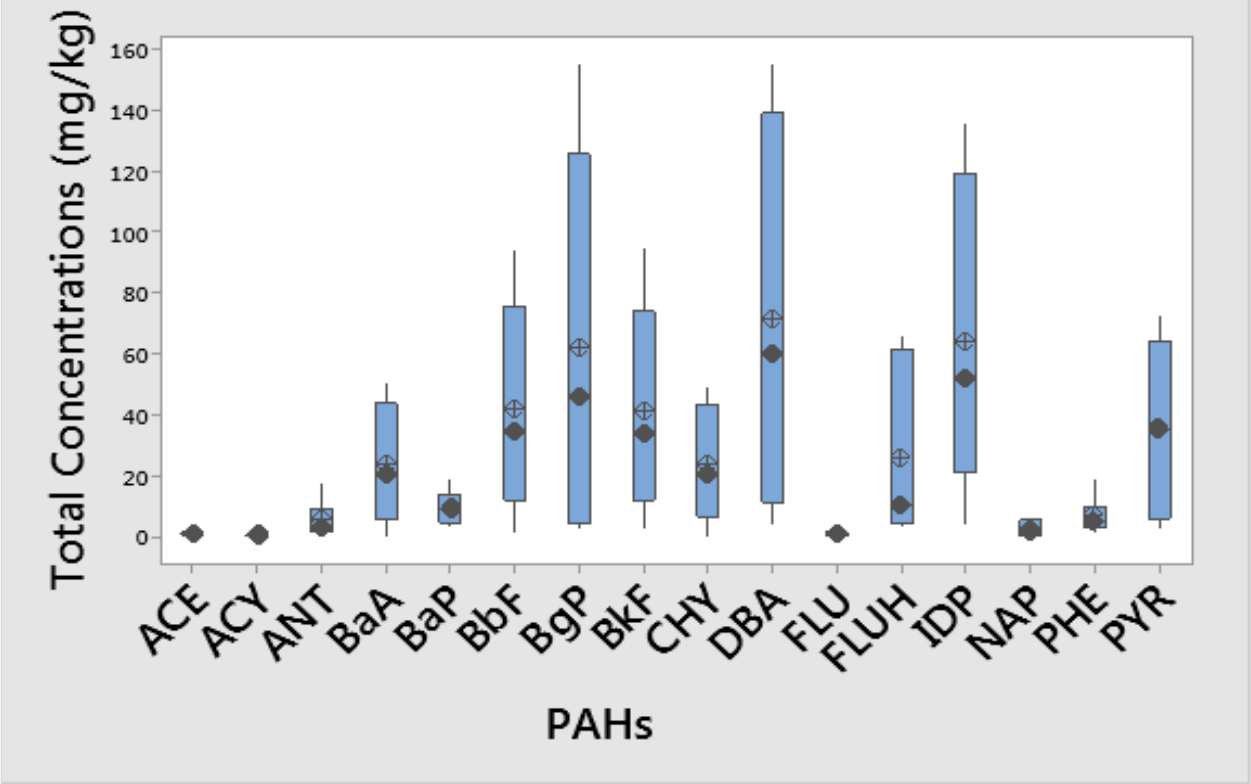

Fig. 3. Boxplot of individual PAH concentrations in Fly Ash samples (6) with median line (50th percentile), mean cross, upper and lower quartile (25th and 75th percentile) and whiskers.

3.3 Bioaccessible Concentrations of PAHs in Fly Ash Samples

The bioaccessible portions for the 16 PAHs, found with the aid of 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 the six (6) fly ash samples from this study are provided in Fig. The % bioaccessibility of total PAHs in all the six (6) fly ash samples (COF, CAF, RDF, LDF, WOF and WTF) from this study are provided in (Figure 4). 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 LDF and WOF that is more bioaccessible in gastric phase. Considering % bioaccessibility of fly ash in this studied 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 of 14.6 % to 63.2 % in 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 shown that FLU has the highest % bioaccessibility of 76.43 % in gastric phase and 58.60 % of FLU in 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 gastric phase and 98.75 of ACE in gastrointestinal phase against lowest % bioaccessibility 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 observed to have the highest bioaccessibility fraction of 87.65 % of BbF in gastric phase and 98.75 % of ACE in 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. Local refined diesel fly ash observed not detected in NAP in both gastric and intestinal phase with the highest % bioaccessible of 103 57 % ACY and 64.29 % ACY in gastric and intestinal phase respectively. The highest % bioaccessibility observed in waste oil fly ash WOF with the value 33.70 % of ACE in gastric phase and 80.95 % ACY whereas, no value was detected in gastric phase and least value of 0.34 % of BaP in gastrointestinal phase. Finally, waste tyres fly ash WTF in this study indicated FLUH with the highest value of 54.86 % in gastric phase and 69.23 % ACY in gastrointestinal phase respectively with the lowest values recorded in ACY BgP 2.77 % in gastric phase and 5.90 % BaP in gastrointestinal phase. Generally, unexpected high bioaccessibility for acenapthylene in almost all the fly ash samples analyzed in both phases compare with other PAHs from this study.

The boxplot of the individual PAHs bioaccessible concentrations from the fly ash samples indicated 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 acenapthylene indicated lowest bioaccessible fractions ranging from 0.08 mg/kg – 0.16 mg/kg. However, boxplot of the individual PAHs bioaccessible concentrations from the fly ash samples indicated benzo[b]fluoranthene has the maximum bioaccessible fractions in gastrointestinal phase ranging from (0.39 mg/kg – 15.82

mg/kg) whilst acenapthylene indicated lowest bioaccessible fractions ranging from (0.16 mg/kg – 0.63 mg/kg).

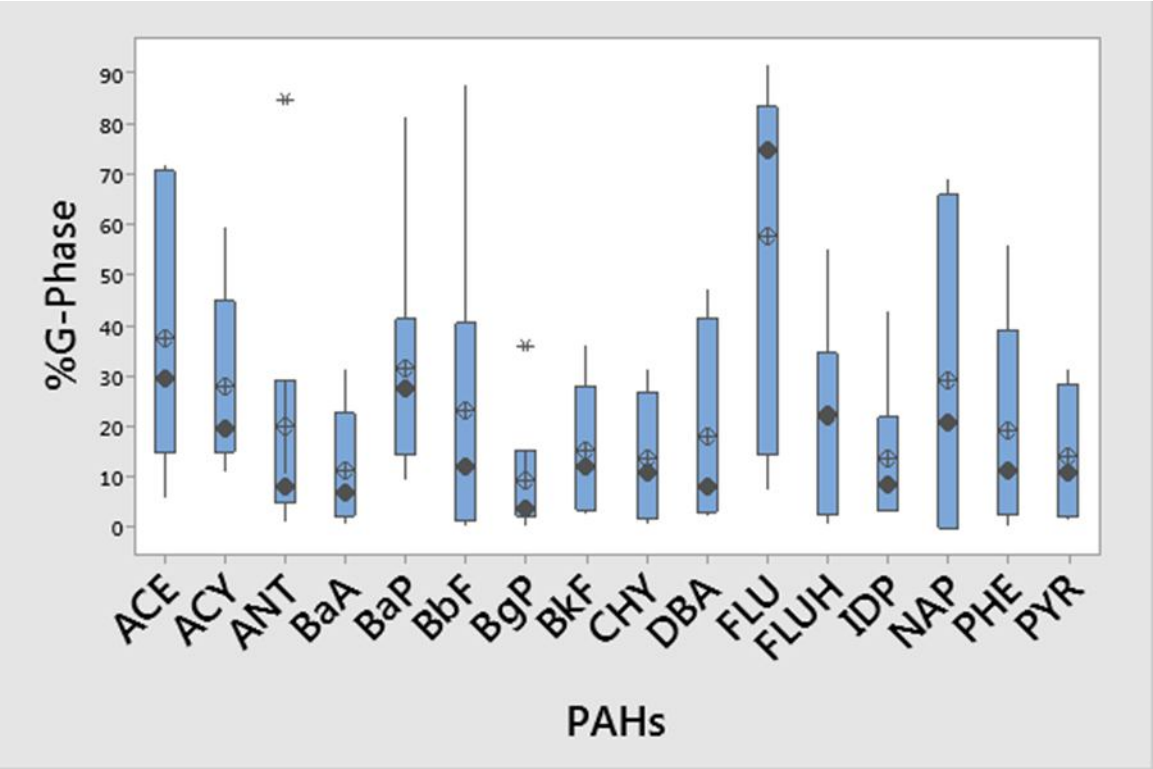

Fig. 4. Boxplot of individual PAH % Bioaccessibility in Gastric Phase from Fly Ash Samples. Where G = Gastric phase

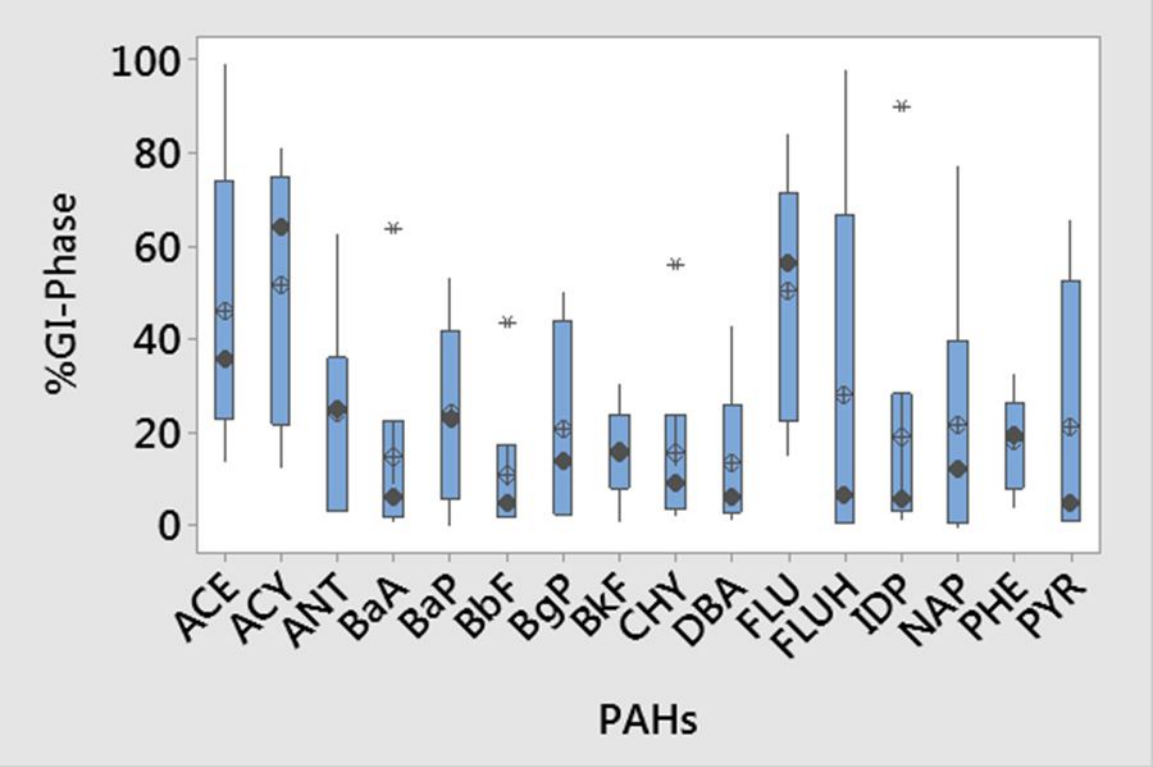

Fig 5. Boxplot of individual PAH % Bioaccessibility in Gastrointestinal Phase from Fly Ash Samples. Where GI = Gastrointestinal phase

The % bioaccesssibility of each individual PAH in fly ash samples shown in (Figure 4 and Figure 5) indicated that % 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 were relatively low, the decrease in bioaccessibility of individual PAHs with increase in the ring number in both gastric and gastrointestinal 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 water and increase in K_{ow} of individual PAHs with increase in number of their benzene ring. Fluorene was the most bioaccessible in gastric phase among all the sixteen PAHs studied in this research which might be as a result that fluorene is highly soluble in water compare with other higher molecular weight PAHs.The same trend of results reported by Lorenzi *et al*. [1]. Acenapthylene was observed to have the highest % bioaccessibility in gastrointestinal phase compare to other PAHs analyzed.

The boxplot of the individual PAHs % bioaccessibility from the fly ash samples in the gastric phase (Figure 4) indicated acenapthylene with the highest upper quarter with the percentage bioaccessibility of about 103 % in gastric phase. Also, some of the maximum upper quartiles bioaccessible portion showed for acenaphthalene, fluorene, naphthalene, anthracene enzo(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 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 gastric phase happened to have the highest % bioaccessibility values, as discussed before. All the compounds analyzed in this study indicated median and mean below 40 % except that of flourene that is above 40 % in gastric phase with the median double the concentrations range.

The individual PAHs % bioaccessibility from the fly ash samples in the gastrointestinal phase also indicated acenaphthalene with the highest upper quarter with the percentage bioaccessibility of about 98.75 % in 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 were in lower quarter range in 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 median below 40 %

except flourene and acenaphthylene. This study also indicated that all the compounds have mean values below 40 % except acenaphthalene, acenaphthylene and fluorene that shown 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 a very relatively high concentrations. The total PAHs concentrations values observed from this study range for the six matrices was 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, local 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 PAHs 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 heath effect from burning tyres, petroleum and its products. The results showed that the fly ash from these product were categorized as heavily contaminated, based on their total concentration of PAHs and bioaccessible percentages fraction of PAHs. Naphthalene, acenaphthylene, acenaphthene, and flourene with 2-3 rings 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 gastric phase while acenaphthalene had the maximum percentage bioaccessibility of 98.75 % in gastrointestinal phase.

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