Original research article

# Concentrations, sources and risk characterisation of polycyclic aromatic hydrocarbons (PAHs) in green, herbal and black tea products in Nigeria

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### A B S T R A C T

This study describes the analysis of 16 + 1 US-EPA Priority PAHs (polycyclic aromatic hydrocarbons) occurrence in twenty-three (23) imported and locally manufactured samples of green, black and herbal tea commercially marketed and widely consumed in Nigeria. A gas chromatograph (GC) coupled with an auto-sampler in tandem with a flame ionisation detector (FID) was used for the analysis. The percentage recoveries of each individual PAH varied between 90.24 and 108.92%. The degree of contamination expressed as sum of sixteen priority PAHs ($\Sigma16$PAHs) ranged between $1.63 \pm 0.33–73.53 \pm 6.07 \mu g/kg$, $4.71 \pm 0.23–79.61 \pm 7.02 \mu g/kg$, and $12.52 \pm 0.15–26.89 \pm 0.68 \mu g/kg$, for green, herbal and black tea samples, respectively. Benzo(a)pyrene played a significant role in the carcinogenicity and mutagenicity potentials of the samples. The lifetime cancer incident risk assessments indicate higher cancer risk levels in herbal and black teas. Generally, children have higher lifetime probability of cancer risk than adults.

## 1. Introduction

In recent years, the rate of tea consumption in Nigeria has increased tremendously. Imported and locally produced tea products, including green, black, Oolong, fruit and herbal (moringa, chamomile, mint) teas, are widely consumed as household beverages, while trends also indicate increased consumption at offices, roadside and mobile kiosks, and bus terminals. On any given day, approximately 60% of the Nigerian population are likely to drink tea. More so, all over the world, tea is the second most consumed non-alcoholic drink, the first being water (Tea Fact sheet, 2014). In the last ten years, the world's tea production has increased, to about 5.35 million tonnes in 2013 according to Food and Agriculture Organization of the United Nations (FAO, 2015). Tea is a refreshing beverage that has several health benefits such as antioxidant effects (da Silva Pinto, 2013; Lee and Foo, 2013; Londoño et al., 2015; Wiseman and Rietveld, 2003), body weight control (Rains et al., 2011), cognitive performance (Jäger and Saaby, 2011), and decrease in cardiovascular disease (Wolfram, 2007).

Tea is widely produced from the plant of the *Theaceae* family known as *Camellia sinensis*. Over the years, several methods have been developed for processing different types of tea. These include the non-oxidised and non-fermented process to produce green tea, and the fully oxidised and fermented method, which results in the production of black tea. Herbal teas are widely produced from well-dried, ground (in some products), and processed roots, stem bark, seeds, or flowers of herbaceous plants, and may not necessarily contain *Camellia sinensis* leaves.

Several research studies have reported on the cumulative tea-drinking cancer reduction potential associated with several brands of tea products (Dora et al., 2003; Hakim et al., 2000; Su and Arab, 2002). Tea (*Camellia sinensis*) leaves contain naturally occurring anti-carcinogenic compounds such as flavonoids, theanine and epigallocatechin gallate (EGCG). However, several recent researches have reported that they also contain inorganic and organic carcinogenic contaminants, such as heavy metals, polycyclic aromatic hydrocarbons (PAHs), and pesticides, that are largely due to inputs from human-mediated activities (Fred-Ahmadu and Benson, 2017; Grover et al., 2013; Li et al., 2011; Lin and Zhu, 2004; Drabova et al., 2012; Pincemaille et al., 2014; Singh et al., 2011; EFSA, 2008).

Polycyclic aromatic hydrocarbons (PAHs) are a class of ubiquitous, persistent and toxic organic chemicals with two or more fused aromatic rings. Tea leaves have been shown to accumulate PAHs *via* aerial deposition from the environment and during processing stages like drying by wood or coal burning (Lin and Zhu, 2004). Due to the enormity of

**Table 1**
General information about the samples used.

| Product name | Code | Country of origin | Flavour | Manufacturer's nutrition facts |
|---|---|---|---|---|
| Ty-phoo Pure Green Tea | TWG | United Kingdom | – | 100% green tea |
| Heladiv Green Tea | HGT | Sri-Lanka | anti-oxidant | total fat 0%, Na 0%, carbohydrate 0%, protein 0% |
| Gold blend Green Tea | GBG | Sri-Lanka | lemon & ginger | energy 0%, Na 0%, anti-oxidants 100–200 mg/200 mL |
| Super blend Green Tea | SBG | Sri Lanka | vanilla | Na 0% |
| Lipton Green Tea | LGB | USA | blackberry pomegranate | total fat 0 g, Na 0 mg, K 5 mg. |
| Lipton Green Tea | LGL | USA | lemon & ginseng | Na 0 mg, K 15 mg |
| Lipton Green Tea | LGR | USA | red goji raspberry | Na 0 mg, K 10 mg |
| Lipton Green Tea | LGJ | USA | jasmine passion with fruits | Na 0 mg, K 10 mg |
| Loyd Green Sense | LGS | Poland | aloe vera | Green tea 77%, white tea 20% |
| Bigelow Green Tea | BGT | USA | decaffeinated, aloe vera | 1–8 mg caffeine |
| Twinings Pure Green Tea | TWG | United Kingdom | – | Green tea |
| Lipton Yellow Label Tea | LYL | Nigeria | – | energy 2 kJ/ < 1 kcal, protein 0.1 g, sugars 0 g, fat 0 g, fibre 0 g, Na 0 g. |
| Natural Liver Flush Tea | NLF | China | – | – |
| Top Tea | TTG | Nigeria | ginger | – |
| Tranquilizing & Brain nourishing Tea | TBN | China | – | – |
| Moringa Herbal Tea | MHT | Nigeria | – | – |
| Sahul Slim Herbal Tea | SSH | India | – | *Garcinia indica* 0.75 g, *Cyperus rotundus* 0.5 g, *Commiphora mukul* 0.6 g, *Garcinia pedunculata* 0.25 g, *Trigonella foenum gracecum* 0.2 g, *Clerodendrum phlomidis* 0.25 g, *Tinospora cordiofolia* 0.25 g, *Emblica officinalis* 0.25 g, *Terminalia chebula* 0.25 g, *Terminalia belerica* 0.25 g, *Zingiber officinale* 0.25 g, *Piper longum* 0.25 g, *Piper nigrum* 0.25 g, *Areca catechu* 0.25 g, *Terminalia arjuna* 0.25 g |
| Anti-hypertensive Tea | AHT | China | – | – |
| Joint Care Tea | JCT | China | – | – |
| Kidney Flush Tea | KFT | China | – | – |
| Anti-Cancer Tea | ACT | China | – | – |
| Top Tea | TTL | Nigeria | lime & lemon | – |
| Top Tea (Regular) | TTR | Nigeria | – | – |

consumption of tea across the world populations, monitoring of PAHs concentrations in tea and the assessment of the associated human and environmental health risks is of high priority. More than one hundred PAHs congeners have been identified in environmental matrices, including air, soil, sediment, water, and food. They are known to possess carcinogenic, mutagenic and teratogenic potentials (McGrath et al., 2007) and, in recent years, there has been heightened health concerns regarding their occurrence food products. PAHs are classified as low molecular weight (LMW) PAHs when they possess a 2–3 fused ring structure and high molecular weight (HMW) when there are 4–6 fused aromatic rings. The LMW PAHs have higher vapour pressure and are found largely in air samples while the HMW PAHs are usually bound to particulates. The latter are more resistant to biodegradation, more toxic and persist longer in the environment (Qi et al., 2014).

PAHs are a product of natural processes, such as volcanic eruption, diagenesis, forest fires, crude oil, shale oil etc. (ATSDR, 1995), and anthropogenic activities, which include coal and wood burning, incomplete combustion of petrol and diesel (Mostert et al., 2010), liquid oil and fuel spills (da Silva and Bicego, 2010). US EPA identified 16 priority PAHs (acenaphthene, ACN, acenaphthylene, ACY, anthracene, ANT, benzo(a)anthracene, BaA, benzo(a)pyrene, BaP, benzo(b)fluoranthene, BbF, benzo(g,h,i)perylene, BghiP, dibenzo(a,h)anthracene, DahA, fluoranthene, FLA, benzo(k)fluoranthene, BkF, chrysene, CHR, indeno(1,2,3cd)pyrene, IP, phenanthrene, PHE, naphthalene, NAP, fluorene, FLR, and pyrene, PYR), which are representative of the hundreds of PAHs in the environment. From these 16 PAHs, EFSA (2008) selected PAH4 (BaP + CHR + BaA + BbF) and PAH8 (PAH4 + BkF + BghiP + DahA + IP) as biomarkers of PAHs occurrence in foods, based on their frequency of occurrence above detection limits in sample matrices. The occurrence of PAHs has been reported in many food items including coffee brew (Orecchio et al., 2009), fruits and vegetables (Camargo and Toledo, 2003), cereals (Orecchio and Papuzza, 2009), fish (Nwaichi and Ntorgbo, 2016), meat (Li et al., 2015), sugar cane

(Silva et al., 2010), and edible oils (Hao et al., 2015). Some studies on the contamination of PAHs in *Camellia sinensis* have been conducted in China (Lin and Zhu, 2004), Germany (Zuin et al., 2005), Spain (García-Falcon et al., 2005), Czech Republic (Drabova et al., 2012), Luxembourg (Pincemaille et al., 2014), Argentina (Londoño et al., 2015) and Brazil (Milani et al., 2016). Several other reports on the contamination of PAHs exist (Adisa et al., 2015; Bishnoi et al., 2005; Ciemniak and Mocek, 2010; Chen et al., 2016; Duedahl-Olesen et al., 2015; Fiedler et al., 2002; Grover et al., 2013; Ishizaki et al., 2010; Iwegbue et al., 2015; Kayali-Sayadi et al., 1998; Khiadani et al., 2013; Li et al., 2011; Pincemaille et al., 2014; Schulz et al., 2014; Shi et al., 2016; Singh et al., 2011). However, this study presents a survey of US EPA 16 + 1 priority PAHs in branded green, black and herbal tea samples commercially sold in Nigeria.

Tea consumption has been identified as an important pathway of human exposure to many contaminants, including PAHs, and therefore, PAH contamination of *Camellia sinensis* and herbal tea may have serious health implications. The objectives of this study include (1) determination of the levels of polycyclic aromatic hydrocarbons (PAHs) in tea samples commercially sold and consumed in Nigeria; (2) identification of the sources of polycyclic aromatic hydrocarbons; (3) evaluation of the level of health risk associated with PAHs exposure through consumption of tea.

## 2. Experimental

### 2.1. Reagents

#### 2.1.1. Analytical PAHs standard

The standard reference solution used was purchased from Accustandard (New Haven, CT) with components as follows: acenaphthene (ACN), acenaphthylene (ACY), anthracene (ANT), benzo(a) anthracene (BaA), benzo(a)pyrene (BaP), benzo(b)fluoranthene, (BbF),

**Table 2a**
Concentrations (Mean ± standard deviation, $n = 3$) of PAH congeners in branded green tea samples.

| Analyte | TPG | HGT | GBG | SBG | LBG | LGL | LGR | LGJ | LGS | BGT | TWG |
|---|---|---|---|---|---|---|---|---|---|---|---|
| NAP | BDL | 0.79 ± 0.02 | 0.34 ± 0.07 | 0.73 ± 0.15 | 0.55 ± 0.26 | BDL | BDL | 0.09 ± 0.02 | 0.15 ± 0.05 | 0.22 ± 0.17 | BDL |
| ACN | BDL | 0.43 ± 0.06 | 0.53 ± 0.09 | 0.52 ± 0.08 | 0.34 ± 0.03 | BDL | BDL | BDL | 0.26 ± 0.06 | BDL | BDL |
| ACY | BDL | 0.29 ± 0.15 | 0.35 ± 0.19 | 0.15 ± 0.16 | 0.64 ± 0.21 | BDL | BDL | BDL | 0.56 ± 0.01 | BDL | BDL |
| FLR | BDL | 0.17 ± 0.12 | 0.534 ± 0.08 | BDL | 0.41 ± 0.09 | BDL | 0.05 ± 0 | BDL | 0.19 ± 0.04 | BDL | BDL |
| PHE | BDL | 0.91 | 0.28 ± 0.06 | BDL | 1.47 ± 0.19 | BDL | BDL | BDL | 0.72 ± 0.17 | BDL | BDL |
| ANT | BDL | BDL | BDL | BDL | 0.96 ± 0.3 | BDL | BDL | BDL | 0.5 ± 0.09 | BDL | BDL |
| CBZ | 0.56 ± 0.05 | 0.86 ± 0.23 | BDL | 0.39 ± 0.09 | 2 ± 0.55 | 0.99 ± 0.12 | 0.67 ± 0.02 | BDL | 0.87 ± 0.03 | 0.27 ± 0.16 | 1.61 ± 0.13 |
| FLA | BDL | BDL | BDL | BDL | 1.98 ± 0.42 | BDL | BDL | BDL | 1.62 ± 0.24 | BDL | BDL |
| PYR | BDL | BDL | BDL | BDL | 0.94 ± 0.42 | BDL | BDL | BDL | 3.79 ± 0.01 | BDL | BDL |
| BaA | BDL | 3.97 ± 0.04 | 2.04 ± 0.25 | 5.25 ± 0.17 | 4.29 ± 0.31 | BDL | BDL | BDL | 9.31 ± 1.39 | 4.47 ± 0.21 | 0.83 ± 023 |
| CHR | BDL | 6.1 ± 0.3 | 3.24 ± 0.08 | 8.43 ± 0.28 | 12.92 ± 0.46 | BDL | BDL | BDL | 26.02 ± 2.46 | 6.96 ± 0.61 | BDL |
| BbF | BDL | 10.26 ± 0.28 | 5.15 ± 0.11 | 14.36 ± 0.13 | 6.35 ± 0.26 | BDL | BDL | BDL | 0.42 ± 0.11 | BDL | BDL |
| BkF | BDL | BDL | BDL | 0.59 ± 0.14 | BDL | BDL | BDL | BDL | 3.3 ± 0.00 | BDL | BDL |
| BaP | BDL | 1.22 ± 0.30 | 1.12 ± 0.15 | 10.05 ± 8.19 | 2.36 ± 0.14 | 1.28 ± 0.41 | 2.83 ± 0.38 | 4.8 ± 0.15 | 8.82 ± 0.12 | 3.73 ± 0.31 | 15.9 ± 0.31 |
| DahA | 1.63 ± 0.33 | 13.17 ± 0.22 | 8.37 ± 0.11 | 12.15 ± 0.63 | 6.88 ± 0.36 | 2.59 ± 0.12 | 2.69 ± 0.79 | 1.86 ± 0.15 | 13.29 ± 0.25 | 9.03 ± 0.13 | 6.71 ± 0.26 |
| BghiP | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL |
| IP | BDL | 5.11 ± 0.56 | 1.77 ± 0.29 | 6.51 ± 0.97 | 3.15 ± 0.45 | BDL | BDL | BDL | 4.57 ± 0.19 | 4.2 ± 0.31 | BDL |
| $\Sigma_{16}$PAHs | 1.63 ± 0.33 | 42.43 ± 0.65 | 23.72 ± 0.4 | 58.74 ± 8.09 | 43.24 ± 1.22 | 3.87 ± 0.33 | 5.59 ± 0.87 | 6.76 ± 0.11 | 73.53 ± 6.07 | 28.61 ± 1.46 | 23.45 ± 0.22 |

ACN = acenaphthene, ACY = acenaphthylene, ANT = anthracene, BaA = benzo(a)anthracene, BaP = benzo(a)pyrene, BghiP = benzo(g,h,i)perylene, BbF = benzo(b)fluoranthene, BkF = benzo(k)fluoranthene, CBZ = carbazole, CHR = chrysene, DahA = dibenzo(a,h)anthracene, FLA = fluoranthene, FLR = fluorene, IP = indeno(1,2,3cd)pyrene, NAP = naphthalene, PHE = phenanthrene, PYR = pyrene; BDL = below detection limit.
The concentration of carbazole (CBZ) is not included in the $\Sigma_{16}$PAHs.

benzo(g,h,i)perylene (BghiP), dibenzo(a,h)anthracene (DahA), fluoranthene (FLA), benzo(k)fluoranthene (BkF), chrysene (CHR), indeno (1,2,3cd)pyrene (IP), phenanthrene (PHE), naphthalene (NAP), fluorene (FLR), pyrene (PYR) and carbazole (CBZ). The standard PAH Calibration Mix used was a 2.0 mg/mL stock solution in dichloromethane:benzene (1:1) (AccuStandard No. Z-014G-R) with individual PAH concentrations: ACN 2002 ± 0.4 µg/mL, ACY 1984 ± 2.1 µg/mL, ANT 1999 ± 3.2 µg/mL, BaA 2003 ± 14.4 µg/mL, BaP 2007 ± 17.1 µg/mL, BbF 2004 ± 1.3 µg/mL, BghiP 1982 ± 4.3 µg/mL, BkF 1987 ± 14.5 µg/mL, CHR 2005 ± 0.8 µg/mL, DahA 1981 ± 4.6 µg/mL, FLA 2000 ± 3.5 µg/mL, FLR 1966 ± 10.4 µg/mL, IP 1997 ± 4.5 µg/mL, NAP 1995 ± 3.4 µg/mL, PHE 2004 ± 0.1 µg/mL, PYR 1983 ± 2.1 µg/mL, and CBZ 1994 ± 2.2 µg/mL.

### 2.1.2. Solvents

The n-hexane used was of GC grade and of highest purity ($\geq 96.0\%$), purchased from Merck (KGaA, Germany). Silica gel (60–200 mesh) was purchased from Loba Chemie (India) while anhydrous sodium sulfate used was sourced from Sigma-Aldrich (Gillingham, UK). Deionised water was used all through the bench work.

### 2.1.3. Instrumentation

PAHs were analysed using an Agilent 7890A gas chromatograph (GC), coupled to flame ionisation detector (FID), with an Agilent 7683B autosampler. The GC was equipped with an Agilent HP-5 column (30 m × 0.32 mm × 0.25 µm). The carrier gas used was helium maintained at a flow rate of 4.84 mL/min. The oven temperature program was as follows: 0.4 min at 50 °C, to 195 °C at 20 °C/min, held for 3.0 min, to 250 °C at 8 °C/min, held for 5.0 min, to 290 °C at 5 °C/min, held for 1.0 min. Helium and nitrogen gases of 99.9999% purity were purchased from Foshan Huate Gas Co. Ltd. (China).

### 2.2. Samples

Twenty three (23) branded tea samples were randomly selected and purchased from retail outlets in Lagos and Ota, Ogun state, Nigeria: eleven (11) green tea, eight (8) herbal tea and four (4) black tea brands as presented in Table 1. Samples were crushed mechanically in the laboratory with mortar and pestle prior to extraction.

### 2.3. PAHs extraction from branded tea samples

The extraction method used is a modification of Vieira et al. (2010) reported by Garcia Londono et al. (2015). Precisely, 0.5 g of tea sample were weighed on an analytical balance and 15 mL of n-hexane were added. The mixture was vortexed (J.P. Selecta, Barcelona, Spain) for 20 s then sonicated (Langford Sonomatic 1400 ultrasonic bath, UK) for 20 min at 60 °C. After the sonication, the mixture was centrifuged at 3000 rpm for 10 min. The supernatant was decanted into a 100-mL flask. Sonication and centrifugation were repeated twice with 10 mL of n-hexane and total supernatant volume was approximately 35 mL. The extract was evaporated at 55 °C to 3 mL in a water bath (Uniscope SM801A laboratory water bath; Surgifield Medical England, Okehampton, UK). This was filtered through filter paper and collected in glass tubes; the 100 mL flask was washed three times with 0.75 mL of n-hexane and filter paper was washed with 1 mL of n-hexane resulting in a total volume of approximately 6.25 mL, which was evaporated in the water bath at 36 °C to a volume of approximately 2 mL.

### 2.4. Clean up and preparation for GC-FID analysis

Silica gel (60–200 mesh) was activated at 130 °C overnight in a hot air oven and cooled in a desiccator at room temperature. Approximately, 3.0 g of the silica gel were weighed and packed into a clean column plugged with cotton wool and set up on a retort stand.

**Table 2b**
Concentrations (Mean ± standard deviation, n = 3) of PAH congeners in branded herbal and black tea samples

| analyte | herbal tea | | | | | | | | black tea | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | NLF | TBN | MHT | SSH | AHT | JCT | KFT | ACT | LYL | TTG | TTL | TTR |
| NAP | 0.14 ± 0.08 | 0.2 ± 0.13 | BDL | 0.36 ± 0.11 | 0.03 ± 0.01 | 0.08 ± 0.03 | 0.15 ± 0.03 | BDL | 0.09 ± 0.03 | 0.22 ± 0.03 | 0.08 ± 0.04 | 0.08 ± 0.04 |
| ACN | BDL | BDL | BDL | 0.66 ± 0.11 | BDL | 0.25 ± 0.11 | BDL | BDL | BDL | BDL | BDL | BDL |
| ACY | BDL | 0.09 ± 0.00 | BDL | 2.25 ± 0.04 | 0.34 ± 0.00 | 1.74 ± 2.65 | BDL | BDL | 0.27 ± 0.09 | 1.61 ± 0.05 | BDL | BDL |
| FLE | BDL | BDL | BDL | 0.43 ± 0.09 | 0.06 ± 0.03 | 4.19 ± 0.11 | BDL | BDL | BDL | 0.13 ± 0.00 | BDL | BDL |
| PHE | BDL | BDL | BDL | 1.92 ± 0.61 | 0.24 ± 0.02 | 4.02 ± 0.29 | BDL | BDL | BDL | BDL | BDL | BDL |
| ANT | BDL | BDL | BDL | 1.98 ± 0.49 | 0.78 ± 0.13 | 0.31 ± 0.03 | BDL | BDL | BDL | BDL | BDL | BDL |
| CBZ | 0.49 ± 0.12 | 0.26 ± 0.11 | BDL | 2.43 ± 1.74 | 0.49 ± 0.09 | 3.12 ± 2.33 | BDL | 0.92 ± 0.26 | 1.98 ± 0.06 | 0.72 ± 0.03 | 0.67 ± 0.14 | 0.44 ± 0.06 |
| FLA | BDL | BDL | BDL | 0.53 ± 0.11 | BDL | 1.08 ± 0.72 | BDL | BDL | 0.58 ± 0.06 | BDL | BDL | BDL |
| PYR | BDL | BDL | BDL | 2.62 ± 0.36 | BDL | 1.95 ± 0.67 | BDL | BDL | BDL | BDL | BDL | BDL |
| BaA | BDL | 4.24 ± 0.14 | BDL | 10.22 ± 0.41 | 1.20 ± 0.03 | 1.10 ± 0.05 | BDL | BDL | 0.82 ± 0.41 | 2.03 ± 0.68 | 2.11 ± 0.07 | BDL |
| CHR | BDL | 6.89 ± 0.11 | BDL | 20.21 ± 0.20 | 2.53 ± 0.31 | 5.37 ± 1.42 | BDL | BDL | 1.48 ± 0.14 | 2.94 ± 0.04 | 3.65 ± 0.27 | 0.89 ± 0.59 |
| BbF | BDL | BDL | BDL | 1.97 ± 1.6 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL |
| BkF | BDL | 0.55 ± 0.00 | BDL | 1.40 ± 0.57 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL |
| BaP | 6.56 ± 0.17 | 11.07 ± 0.49 | 0.76 ± 0.00 | 1.91 ± 0.26 | 8.48 ± 0.16 | 28.35 ± 0.35 | 4.03 ± 0.19 | 8.4 ± 0.10 | 2.04 ± 0.15 | 6.22 ± 0.03 | 2.75 ± 0.30 | 5.21 ± 0.26 |
| DahA | 1.22 ± 0.22 | 10.19 ± 0.18 | 3.44 ± 0.07 | 28.24 ± 0.64 | 10.75 ± 0.47 | 1.75 ± 0.17 | 0.53 ± 0.00 | 6.41 ± 0.57 | 8.99 ± 0.32 | 11.91 ± 0.25 | 8.57 ± 0.24 | 6.33 ± 0.43 |
| BghiP | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL |
| IP | BDL | 3.79 ± 0.74 | 0.82 ± 0.00 | 4.88 ± 6.25 | 1.48 ± 0.26 | BDL | BDL | BDL | BDL | 1.82 ± 0.16 | 1.99 ± 0.20 | BDL |
| $\Sigma_{16}$PAHs | 7.92 ± 0.30 | 37.03 ± 0.35 | 5.03 ± 0.84 | 79.61 ± 7.02 | 25.90 ± 0.76 | 50.21 ± 2.19 | 4.71 ± 0.23 | 14.81 ± 0.54 | 14.28 ± 0.62 | 26.89 ± 0.68 | 19.16 ± 0.39 | 12.52 ± 0.15 |

ACN = acenaphthene, ACY = acenaphthylene, ANT = anthracene, BaA = benzo(a)anthracene, BaP = benzo(a)pyrene, BbF = benzo(b)fluoranthene, BghiP = benzo(g,h,i)perylene, BkF = benzo(k)fluoranthene, CBZ = carbazole, CHR = chrysene, DahA = dibenzo(a,h)anthracene, FLA = fluoranthene, FLR = fluorene, IP = indeno(1,2,3cd)pyrene, NAP = naphthalene, PHE = phenanthrene, PYR = pyrene; BDL = Below detection limit.
The concentration of carbazole (CBZ) is not included in the $\Sigma_{16}$PAHs.

**Table 3**
Comparison of results obtained in similar studies.

| Type of tea | Country | Samples | min–max, µg/kg | | | | | References |
|---|---|---|---|---|---|---|---|---|
| | | | BaA | CHR | BbF | BaP | ΣPAH4 | |
| Green Tea | Argentina | 14 | 0.7–74.4 | 29.6 | 0.15–66.6 | 0.4–61.3 | 8.0–355.9 | Garcia Londono et al. (2015) |
| | Austria | 1 | 15.7 | – | 25.3 | 3.1 | 73.7 | Schlemitz and Pfannhauser (1997) |
| | China | 2 | 16.3–23.5 | 24.9–47.6 | – | 7.4–9.7 | 59.4–101.2 | Fiedler et al. (2002) |
| | China | 4 | – | – | 10.8–20.4 | Nd–23.0 | – | Li et al. (2011) |
| | Czech Republic | 18 | 0.7–28.3 | 2.9–42.4 | 0.7–23.9 | 0.2–17.9 | 4.5–102.3 | Drabova et al. (2012) |
| | Germany | 11 | 1.8–40.4 | 6.7–61.5 | 2.2–33.4 | 1.6–32.6 | 12.3–167.9 | Ziegenhals et al. (2008) |
| | Spain | 17 | – | – | – | 10.24–30.4 | – | Fontcuberta et al. (2006) |
| | Brazil | 1 | 4.2 | 15.9 | – | – | 20.1 | Kamangar et al. (2008) |
| | Nigeria | 11 | 2.04–9.31 | 0.83–26.02 | 0.42–14.36 | 1.12–15.9 | 1.28–44.57 | This study |
| Black Tea | Argentina | 27 | 0.2–62.8 | 2.5–109.1 | 0.1–67.6 | 0.2–92.5 | 4.1–332.0 | Garcia Londono et al. (2015) |
| | Austria | 4 | 0.7–31.9 | 2.0–45.4 | 1.9–22.0 | 0.4–5.9 | 5.0–1.3.7 | Schlemitz and Pfannhauser (1997) |
| | China | 1 | – | – | – | 9.4 | – | Li et al. (2011) |
| | China | 1 | 175.0 | 241.0 | 37.6 | 39.7 | 811.6 | Lin et al. (2005) |
| | Czech Republic | 18 | 1.4–196.1 | 3.9–229.0 | 0.9–123.2 | 0.2–151.7 | 7.4–699.4 | Drabova et al. (2012) |
| | Germany | 11 | 1.3–13.1 | 3.4–18.1 | 1.5–8.1 | 0.8–14.1 | 9.0–44.6 | Ziegenhals et al. (2008) |
| | Japan | 4 | 4.3–44.5 | 5.5–51.7 | 5.2–35.7 | 5.3–73.2 | 21.9–205.1 | Ishizaki et al. (2010) |
| | India | 1 | – | – | 210.4 | 1574.1 | 3569.0 | Grover et al. (2013) |
| | Nigeria | 4 | 0.82–2.11 | 0.89–3.65 | – | 2.04–6.22 | 4.34–11.2 | This study |
| Herbal Tea | Nigeria | 8 | 0–10.22 | 0–20.21 | 0–1.97 | 0.76–28.35 | 0.76–34.8 | This study |

**Table 4**
Mass distribution percentages of PAHs in tea samples.

| type of tea | sample code | mean concentration (Σ₁₆PAH) (µg/kg) | | mass distribution percentage (%) | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | 2- ring | 3- ring | 4- ring | 5- ring | 6- ring |
| green tea | TPG | 1.63 ± 0.33 | 0.00 | 0.00 | 0.00 | 100.00 | 0.00 |
| | HGT | 42.43 ± 0.65 | 1.87 | 4.25 | 23.7 | 58.10 | 12.04 |
| | GBG | 23.72 ± 0.4 | 1.45 | 7.17 | 22.3 | 61.70 | 7.45 |
| | SBG | 58.74 ± 8.09 | 1.24 | 1.13 | 2.30 | 63.30 | 11.00 |
| | LBG | 43.24 ± 1.22 | 1.26 | 8.81 | 45.6 | 36.07 | 7.30 |
| | LGL | 3.87 ± 0.33 | 0.00 | 0.00 | 0.00 | 100.00 | 0.00 |
| | LGR | 5.59 ± 0.87 | 0.00 | 0.99 | 0.00 | 99.00 | 0.00 |
| | LGJ | 6.76 ± 0.11 | 1.43 | 0.00 | 0.00 | 98.60 | 0.00 |
| | LGS | 73.53 ± 6.07 | 0.20 | 3.02 | 55.40 | 6.22 | 6.22 |
| | BGT | 28.61 ± 1.46 | 0.76 | 0.00 | 39.90 | 44.60 | 14.70 |
| | TWG | 23.45 ± 0.22 | 0.00 | 0.00 | 3.53 | 96.50 | 0.00 |
| herbal tea | NLF | 7.92 ± 0.30 | 1.73 | 0.00 | 0.00 | 98.30 | 0.00 |
| | TBN | 37.03 ± 0.35 | 0.55 | 0.24 | 30.10 | 58.90 | 10.20 |
| | MHT | 5.03 ± 0.84 | 0.00 | 0.24 | 0.00 | 83.70 | 16.30 |
| | SSH | 79.61 ± 7.02 | 0.46 | 9.10 | 42.20 | 42.10 | 6.13 |
| | AHT | 25.90 ± 0.76 | 0.11 | 5.52 | 14.40 | 74.20 | 5.72 |
| | JCT | 50.21 ± 2.19 | 0.17 | 20.9 | 18.90 | 59.90 | 0.00 |
| | KFT | 4.71 ± 0.23 | 3.30 | 0.00 | 0.00 | 96.70 | 0.00 |
| | ACT | 14.81 ± 0.54 | 0.00 | 0.00 | 0.00 | 100.00 | 0.00 |
| black tea | LYL | 14.28 ± 0.62 | 0.68 | 1.90 | 20.10 | 77.30 | 0.00 |
| | TTG | 26.89 ± 0.68 | 0.82 | 6.49 | 18.50 | 67.40 | 6.77 |
| | TTL | 19.16 ± 0.39 | 0.40 | 0.00 | 30.10 | 59.10 | 10.40 |
| | TTR | 12.52 ± 0.15 | 0.67 | 0.00 | 7.13 | 92.20 | 0.00 |

Anhydrous $Na_2SO_4$ (1.0 g) of was added to the top of the silica gel, and then 5–10 mL of *n*-hexane were used to condition the column. The sample was introduced into the column, and then eluted with *n*-hexane. The eluent collected was then concentrated to 2 mL using a rotary evaporator. The following seventeen PAHs were determined: acenaphthene (ACN), acenaphthylene (ACY), anthracene (ANT), benzo(a) anthracene (BaA), benzo(a)pyrene (BaP), benzo(b)fluoranthene, (BbF), benzo(g,h,i)perylene (BghiP), dibenzo(a,h)anthracene (DahA), fluoranthene (FLA), benzo(k)fluoranthene (BkF), chrysene (CHR), indeno (1,2,3cd)pyrene (IP), phenanthrene (PHE), naphthalene (NAP), fluorene (FLR), pyrene (PYR) and carbazole (CBZ).

## 2.5. Quality control

The limit of detection (LOD) and limit of quantitation (LOQ) were

calculated as three and ten times the standard deviation of the blanks, respectively. The LOD and LOQ obtained were 0.30 µg/kg and 0.9 µg/ kg, respectively, for each of the four regulated PAHs (BaA, BaP, BbF and CHR). The recoveries of each individual PAH varied from 90.24 to 108.92% for PHE and DahA, respectively. PAH solutions containing 5, 10, 20, 30, 40, and 50 µg/L of stock solution were used to prepare calibration curves. Calibration curves for all analysed PAH standards ($n = 6$) had values of residual standard deviations (RSD) that ranged between 77.02 and 100.60%, demonstrating good repeatability for the analytical method. Triplicate determinations were made on all extracted tea samples.

## 2.6. Lifetime cancer exposure

The probability that a Nigerian is likely to develop cancer from the

**Table 5**
PAH diagnostic ratios (*r*PAH).

| type of tea | sample code | $\frac{FLA}{(FLA + PYR)}$ | | $\frac{BaA}{(BaA + CHR)}$ | |
|---|---|---|---|---|---|
| | | value | sources | value | sources |
| green tea | TPG | 0.00 | – | 0.00 | – |
| | HGT | 0.00 | – | 0.39 | vehicular emission |
| | GBG | 0.00 | – | 0.38 | vehicular emission |
| | SBG | 0.00 | – | 0.38 | vehicular emission |
| | LBG | 0.67 | grass, wood, coal combustion | 0.24 | biomass combustion |
| | LGL | 0.00 | – | 0.00 | – |
| | LGR | 0.00 | – | 0.00 | – |
| | LGJ | 0.00 | – | 0.00 | – |
| | LGS | 0.29 | petrogenic | 0.26 | biomass combustion |
| | BGT | 0.00 | – | 0.39 | vehicular emission |
| | TWG | 0.00 | | 0.00 | |
| herbal tea | NLF | 0.00 | – | 0.00 | – |
| | TBN | 0.00 | – | 0.40 | vehicular emission |
| | MHT | 0.00 | – | 0.00 | – |
| | SSH | 0.16 | petrogenic | 0.33 | biomass combustion |
| | AHT | 0.00 | – | 0.32 | biomass combustion |
| | JCT | 0.35 | petrogenic | 0.17 | petrogenic |
| | KFT | 0.00 | – | 0.00 | – |
| | ACT | 0.00 | – | 0.00 | – |
| black tea | LYL | 0.00 | – | 0.35 | biomass combustion |
| | TTG | 0.00 | – | 0.41 | vehicular emission |
| | TTL | 0.00 | – | 0.36 | vehicular emission |
| | TTR | 0.00 | – | 0.00 | |

consumption of green, herbal and black tea over a lifetime was estimated by calculating the lifetime average daily dose (LADD) and Risk Index ($R_I$) for oral ingestion pathway for two populations, namely children (1–18 years) and adults (above 18 years) using the equations:

$$LADD = \frac{C \times IR \times ER \times ED}{Bw \times AT_n} \tag{iii}$$

where *C* is the concentration of individual PAHs (in mg/kg); *IR* is the ingestion rate (mg/day), *ER* is the exposure rate or exposure frequency (days/year), *ED* is the exposure duration (year), *Bw* is the estimated average body weight (kg), and $AT_n$ is the averaging time i.e. exposure duration $\times$ 365 days. The average body weights of children and adults in Nigeria are estimated to be 48 kg and 70 kg, respectively (Abubakar et al., 2015; Benson et al., 2016a,b). The *IR* values for adults and children are estimated at 2.0 g per day while the *ED* is estimated at 52.5 years (World Bank 2013 estimate for life expectancy in Nigeria; World Bank, 2014).

The lifetime incidence rates or risk index ($RI_i$) of developing cancer from exposure to PAHs was calculated using *Equation iv*. In addition, the total potential cancer risk ($\Sigma RI_i$) from PAHs exposure through oral ingestion was calculated using an additive model as shown in *Equation v* below:

$$RI_i = LADD_i \times SF_i \tag{iv}$$

$$\Sigma RI_i = \Sigma(LADD_i \times SF_i) \tag{v}$$

where SF = slope factor, $RI_i$ = individual PAH risk index, and

$\Sigma RI_i$ = the sum total of all risk indices for the PAH concentrations in each sample.

### 2.7. Statistical analysis

All data were analysed using XLSTAT-Pro software (AddinSoft, Inc., New York, NY) and Microsoft Excel 2011. Continuous summary descriptives were computed.

## 3. Results and discussion

### 3.1. Levels of polycyclic aromatic hydrocarbons (PAHs)

Tables 2a and 2b present the mean concentrations of individual PAHs in green, herbal and black tea samples investigated in the present study. PAHs concentrations varied greatly and individual levels were largely due to the type of tea and by implication the processes involved in the cultivation, processing and manufacturing of each branded tea sample. DahA, BaP and carbazole were present in 100, 91.30 and 78.26% of samples, respectively, while BghiP was not found in any of the tea samples. The mean concentrations of $\Sigma_{16}$PAHs in green tea samples varied between 1.63 $\pm$ 0.33 and 73.53 $\pm$ 6.07 µg/kg in TPG and LGS samples, respectively. Concentrations of $\Sigma_{16}$PAHs in herbal and black tea samples varied from 4.71 $\pm$ 0.23 to 79.61 $\pm$ 7.02 µg/kg, and 12.52 $\pm$ 0.15 to 26.89 $\pm$ 0.68 µg/kg, respectively. The results indicate that the lowest mean $\Sigma_{16}$PAHs was obtained for the TPG samples.

Green teas are usually subjected to minimal oxidation and drying processes, and are therefore expected to be minimally exposed to PAHs contamination. The present results show LGS, SBG, LBG and HGT with relatively high mean $\Sigma_{16}$PAHs concentrations of 73.53, 58.74, 43.24 and 42.43 µg/kg, respectively. The results indicate that these tea samples accumulated enhanced levels of PAHs possibly from the soil, long-range transport in dense traffic, or aerial deposition (Fahnrich et al., 2002). The age of leaves collected and topography of the cultivation area are other factors that may have influenced the relatively high PAHs concentrations (Malik et al., 2013). The concentrations of $\Sigma_{16}$PAHs in green tea increased in the following order: TPG < LGL < LGR < LGJ < TWG < GBG < BGT < HGT < LBG < SBG < LGS. This trend indicates that LGS, a product of Poland has the highest mean $\Sigma_{16}$PAHs concentration of 73.53 µg/kg followed by SBG (58.74 µg/kg), while TPG has the lowest concentration of 1.63 µg/kg of all the green tea samples investigated.

The highest $\Sigma_{16}$PAHs concentration of 79.61 µg/kg for the herbal tea was detected in SSH which is a slim tea produced in India, and the lowest being KFT (4.71 µg/kg) as shown in Table 2b. The high concentrations of PAHs detected in SSH may be due to the large number of additives present in the product contributing individually to the total PAH content of the sample. This is similar to the findings reported by Cacho et al. (2014), where the highest concentration of PAHs in their study was found in a camomile tea (herbal tea) with a total PAHs concentration of 30 µg/L.

The concentrations for the black tea in this study are significantly lower than some brands of green and herbal teas samples. The highest $\Sigma_{16}$PAHs concentration for black tea was recorded for TTG (26.89 µg/kg). This is consistent with a similar study reported by Ziegenhals et al. (2008). This may also imply that the black tea samples might not have been exposed to PAHs contamination during fermentation and drying. Alternative sources of energy may have been used rather than flame firing or smoking in their production process (Pincemaille et al., 2014).

Table 3 highlights the comparison between the results obtained from this study and that of similar studies across different parts of the world. The manufacturing process of black tea involves withering, rolling, fermentation or full oxidation and drying; the drying process is usually carried out with combustion gases from burning wood, oil or

**Table 6**
Estimated daily intake and risk index assessment of PAH congeners in branded green tea samples.

| analyte | TPG | HGT | GBG | SBG | LBG | LGL | LGR | LGJ | LGS | BGT | TWG |
|---|---|---|---|---|---|---|---|---|---|---|---|
| NAP | 0 | 2.71E-05 (1.86E-05) | 1.18E-05 (8.07E-06) | 2.50E-05 (1.71E-05) | 1.87E-05 (1.28E-05) | 0 (0) | 0 (0) | 3.30E-06 (2.26E-06) | 5.10E-06 (3.50E-06) | 7.46E-06 (5.12E-06) | 0 (0) |
| ACN | 0 | 1.49E-05 (1.02E-05) | 1.83E-05 (1.26E-05) | 1.77E-05 (1.22E-05) | 1.16E-05 (7.93E-06) | 0 (0) | 0 (0) | 0 (0) | 8.76E-06 (6.01E-06) | 0 (0) | 0 (0) |
| ACY | 0 | 9.88E-05 (6.77E-06) | 1.18E-05 (8.12E-06) | 5.08E-06 (3.48E-06) | 2.18E-05 (1.49E-05) | 0 (0) | 0 (0) | 0 (0) | 1.91E-05 (1.31E-05) | 0 (0) | 0 (0) |
| FLR | 0 | 5.68E-05 (3.89E-06) | 1.84E-05 (1.26E-05) | 0 (0) | 1.39E-05 (9.54E-06) | 0 (0) | 1.90E-06 (1.30E-06) | 0 (0) | 6.63E-06 (4.54E-06) | 0 (0) | 0 (0) |
| PHE | 0 | 3.13E-05 (2.15E-05) | 9.71E-06 (6.66E-06) | 0 (0) | 5.03E-05 (3.45E-05) | 0 (0) | 0 (0) | 0 (0) | 2.45E-05 (1.68E-05) | 0 (0) | 0 (0) |
| ANT | 0 | 0 (0) | 0 (0) | 0 (0) | 3.29E-05 (2.26E-05) | 0 (0) | 0 (0) | 0 (0) | 1.71E-05 (1.17E-05) | 0 (0) | 0 (0) |
| CBZ | 6.60E-06 (3.85E-05) | 2.93E-05 (2.01E-05) | 0 (0) | 1.34E-05 (9.21E-06) | 6.87E-05 (4.71E-05) | 3.37E-05 (2.32E-05) | 2.28E-05 (1.56E-05) | 0 (0) | 2.99E-05 (2.05E-05) | 9.12E-06 (6.25E-06) | 5.51E-05 (3.78E-05) |
| FLA | 0 | 0 (0) | 0 (0) | 0 (0) | 6.78E-05 (4.66E-05) | 0 (0) | 0 (0) | 0 (0) | 5.54E-05 (3.80E-05) | 0 (0) | 0 (0) |
| PYR | 0 | 0 (0) | 0 (0) | 0 (0) | 3.23E-05 (2.22E-05) | 0 (0) | 0 (0) | 0 (0) | 1.29E-04 (8.91E-05) | 0 (0) | 0 (0) |
| BaA | 0 | 1.36E-04 (9.33E-05) | 6.99E-05 (4.79E-05) | 1.79E-04 (1.23E-04) | 1.47E-04 (1.01E-04) | 0 (0) | 0 (0) | 0 (0) | 3.19E-04 (2.19E-04) | 1.53E-04 (1.05E-04) | 0 (0) |
| CHR | 0 | 2.09E-04 (1.43E-04) | 1.11E-04 (7.60E-05) | 2.89E-04 (1.98E-04) | 4.43E-04 (3.03E-04) | 0 (0) | 0(0) | 0 (0) | 8.91E-04 (6.11E-04) | 2.38E-04 (1.63E-04) | 2.83E-05 (1.94E-05) |
| BbF | 0 | 3.52E-04 (2.41E-04) | 1.76E-04 (1.21E-04) | 4.92E-04 (3.37E-04) | 2.17E-04 (1.49E-04) | 0 (0) | 0 (0) | 0 (0) | 1.43E-05 (9.79E-06) | 0 (0) | 0 (0) |
| BkF | 0 | 0 (0) | 0 (0) | 2.04E-05 (1.40E-05) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 1.13E-04 (7.75E-05) | 0 (0) | 0 (0) |
| BaP | 0 | 4.17E-05 (2.86E-05) | 3.83E-05 (2.63E-05) | 3.44E-04 (2.36E-04) | 8.09E-05(5.55E-05) | 4.38E-05 (3.00E-05) | 9.70E-05 (6.65E-05) | 1.64E-04 (1.13E-04) | 3.02E-04 (2.07E-04) | 1.28E-04 (8.76E-05) | 5.45E-04 (3.73E-04) |
| DahA | 1.92E-05 (1.12E-04) | 4.51E-04 (3.09E-04) | 2.86E-04 (1.96E-04) | 4.16E-04 (2.85E-04) | 2.36E-04 (1.62E-04) | 8.88E-05 (6.09E-05) | 9.24E-05 (6.34E-05) | 6.37E-05 (4.37E-05) | 4.55E-04 (3.12E-04) | 3.09E-04 (2.12E-04) | 2.29E-04 (1.58E-04) |
| BghiP | 0 | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) |
| IP | 0 | 1.75E-04 (1.19E-04) | 6.05E-05 (4.15E-05) | 2.23E-04 (1.53E-04) | 1.08 E-04 (7.40E-05) | 0 (0) | 0 (0) | 0 (0) | 1.56E-04 (1.07E-04) | 1.44E-04 (9.87E-05) | 0 (0) |
| ΣRI | 1.40E-04 (8.17E-04) | 4.08E-03 (2.80E-03) | 2.59E-03 (1.78E-03) | 6.20E-03 (4.26E-03) | 2.66E-03 (1.82E-03) | 9.68E-04 (6.64E-04) | 1.38E-04 (9.48E-04) | 1.67E-03 (1.14E-03) | 5.90E-03 (4.05E-03) | 3.41E-03 (2.33E-03) | 5.65E-03 (3.87E-03) |

ACN = acenaphthene,    ACY = acenaphthylene,    ANT = anthracene,    BaA = benzo(a)anthracene,    BaP = benzo(a)pyrene,    BbF = benzo(b)fluorthene,    BghiP = benzo(g,h,i)perylene,    BkF = benzo(k)fluoranthene.    CBZ = carbazole, CHR = chrysene, DahA = dibenzo(a,h)anthracene, FLA = fluoranthene, FLR = fluorene, IP = indeno(1,2,3cd)pyrene, NAP = naphthalene, PHE = phenanthrene, PYR = pyrene.

**Table 7**
Estimated daily intake and risk index assessment of PAH congeners in branded herbal and black tea samples.

| analyte | herbal tea | | | | | | | | black tea | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | TBN | TBN | MHT | SSH | AHT | JCT | KFT | ACT | LYL | TTG | TTL | TTR |
| NAP | 4.70E-06 (3.22E-06) | 6.94E-06 (4.76E-06) | 0(0) | 1.25E-05 (8.54E-06) | 1.00E-06 (6.89E-07) | 2.84E-06 (1.95E-06) | 5.29E-06 (3.63E-06) | 0 (0) | 3.33E-06 (2.28E-06) | 7.58E-06 (5.20E-06) | 2.65E-06 (1.82E-06) | 2.85E-06 (1.96E-06) |
| ACN | 0 (0) | 0 (0) | 0 (0) | 2.28E-05 (1.57E-05) | 0 (0) | 8.63E-06 (5.92E-06) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) |
| ACY | 0 (0) | 3.05E-06 (2.09E-06) | 0 (0) | 7.69E-05 (5.28E-05) | 1.17E-05 (8.04E-06) | 5.97E-05 (4.09E-05) | 0 (0) | 0 (0) | 9.13E-06 (6.38E-06) | 5.53E-05 (3.79E-05) | 0 (0) | 0 (0) |
| FLE | 0 (0) | 3.42E-10 (2.35E-10) | 0 (0) | 1.48E-05 (1.02E-05) | 2.01E-06 (1.38E-06) | 1.44E-04 (9.85E-05) | 0 (0) | 0 (0) | 0 (0) | 4.51E-06 (3.09E-06) | 0 (0) | 0 (0) |
| PHE | 0 (0) | 0 (0) | 0 (0) | 6.57E-05 (4.50E-05) | 8.42E-06 (5.78E-06) | 1.38E-04 (9.43E-05) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) |
| ANT | 0 (0) | 0 (0) | 0 (0) | 6.77E-05 (4.64E-05) | 2.68E-05 (1.84E-05) | 1.06E-05 (7.29E-06) | 0 (0) | 0(0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) |
| CBZ | 1.68E-05 (1.15E-05) | 8.93E-06 (6.12E-06) | 0 (0) | 8.33E-05 (5.71E-05) | 1.69E-05 (1.16E-05) | 1.07E-04 (7.33E-05) | 0 (0) | 3.15E-05 (2.16E-05) | 6.78E-05 (4.65E-05) | 2.47E-05 (1.69E-05) | 2.31E-05 (1.58E-05) | 1.52E-05 (1.04E-05) |
| FLA | 0 (0) | 0 (0) | 0 (0) | 1.83E-05(1.25E-05) | 0 (0) | 3.71E-05(2.55E-05) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) |
| PYR | 0 (0) | 0 (0) | 0 (0) | 8.98E-05 (6.16E-05) | 0 (0) | 6.69E-05 (4.58E-05) | 0 (0) | 0 (0) | 1.97E-05 (1.35E-05) | 0 (0) | 0 (0) | 0 (0) |
| BaA | 0 (0) | 1.45E-04 (9.96E-05) | 0 (0) | 3.49E-04 (2.40E-04) | 4.10E-05 (2.81E-05) | 3.78E-05 (2.59E-05) | 0 (0) | 0 (0) | 2.81E-05 (1.92E-05) | 6.96E-05 (4.77E-05) | 7.25E-05 (4.97E-05) | 0 (0) |
| CHR | 0 (0) | 2.36E-04 (1.62E-04) | 0 (0) | 6.92E-04 (4.75E-05) | 8.67E-05 (5.95E-05) | 1.84E-04 (1.26E-04) | 0 (0) | 0 (0) | 5.07E-05 (3.48E-05) | 1.01E-04 (6.92E-05) | 1.25E-04 (8.57E-05) | 3.06E-05 (2.10E-05) |
| BbF | 0 (0) | 0 (0) | 0 (0) | 6.75E-05 (4.63E-05) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) |
| BkF | 0 (0) | 1.87E-05 (1.28E-05) | 0 (0) | 4.81E-05 (3.30E-05) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) |
| BaP | 2.25E-04 (1.54E-04) | 3.79E-04 (2.60E-04) | 2.62E-05 (1.80E-05) | 6.54E-05 (4.49E-05) | 2.90E-04 (1.99E-04) | 9.71E-04 (6.66E-04) | 1.38E-04 (9.46E-05) | 2.88E-04 (1.97E-04) | 6.99E-05 (4.79E-05) | 2.13E-04 (1.46E-04) | 9.42E-05 (6.46E-05) | 1.79E-04 (1.22E-04) |
| DahA | 4.18E-05 (2.87E-05) | 3.49E-04 (2.39E-04) | 1.18E-04 (8.09E-05) | 9.67E-04 (6.63E-04) | 3.68E-04 (2.52E-04) | 5.99E-05 (4.11E-05) | 1.81E-05 (1.24E-05) | 2.19E-04 (1.50E-04) | 3.08E-04 (2.11E-04) | 4.08E-04 (2.80E-04) | 2.93E-04 (2.01E-04) | 2.17E-04 (1.49E-04) |
| BghiP | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 0 (0) |
| IP | 0 (0) | 1.30E-04 (8.91E-05) | 2.81E-05 (1.93E-05) | 1.67E-04 (1.15E-04) | 5.08E-05 (3.49E-05) | 0 (0) | 0 (0) | 0 (0) | 0 (0) | 6.24E-05 (4.28E-05) | 6.84E-05 (4.69E-05) | 0 (0) |
| ΣRI | 1.94E-03 (1.33E-03) | 5.52E-03 (3.79E-03) | 1.07E-03 (7.36E-04) | 7.97E-03 (5.47E-03) | 4.87E-03 (3.34E-03) | 7.55E-03 (5.18E-03) | 1.14E-03 (7.81E-04) | 3.70E-03 (2.54E-03) | 2.78E-03 (1.91E-03) | 4.63E-03 (3.17E-03) | 2.93E-03 (2.02E-03) | 2.89E-03 (1.98E-03) |

ACN = acenaphthene, ACY = acenaphthylene, ANT = anthracene, BaA = benzo(a)anthracene, BaP = benzo(a)pyrene, BbF = benzo(b)fluoranthene, BghiP = benzo(g,h,i)perylene, BkF = benzo(k)fluoranthene, CBZ = carbazole, CHR = chrysene, DahA = dibenzo(a,h)anthracene, FLA = fluoranthene, FLR = fluorene, IP = indeno(1,2,3cd)pyrene, NAP = naphthalene, PHE = phenanthrene, PYR = pyrene.

coal, which introduces very high levels of PAHs (Lin and Zhu, 2004). Consequently, black teas are expected to exhibit high concentrations of PAHs. Generally, the results from Table 3 show black teas as being more contaminated with PAHs than green and herbal teas. The present results are comparable with similar reports from other parts of the world.

### 3.2. Mass distribution percentage

Table 4 shows the mass distribution of 2- to 6-ring PAHs in green, black and herbal teas as a percentage of the total PAHs in the products investigated. The distribution shows a predominance of the 5-membered ring structures (BaP, BbF, BkF, DahA) with percentages ranging from 35.14% for LGS to 100% for TPG, LGL and ACT, respectively. Four-membered ring PAHs (FLA, PYR, BaA, CHR) were dominant in all LGS samples. In general, most green tea samples were dominated by 5-membered ring PAHs, while LGL, LGR, LGJ, and TWG samples indicate zero to insignificant contributions of 2-, 3- and 6-membered aromatic hydrocarbon rings. This is indicative of the persistence, chemical stability, ability to sorb to particles or solids, and non-biodegradability of the 4- and 5-membered rings group of PAHs, which are classified as HMW PAHs. The predominance of HMW-PAHs may also be due to the fact that LMW-PAHs are preferentially degraded during PAH transport and depositional flux. This finding is consistent with the existing literature on PAHs (Lin and Zhu, 2004; Londoño et al., 2015). Among the herbal tea samples, SSH presented an almost equal composition of its 4- and 5-membered rings, of 42.2% and 42.1%, respectively. These HMW PAHs are known to be more toxic than the LMW 2- and 3-membered rings, which are more volatile. This means that consumption of these products with relatively high percentage of 4- and 5-membered ring hydrocarbons might likely impart undesirable health risks to consumers.

### 3.3. PAH diagnostic ratios

The PAHs diagnostic ratios (rPAHs) considered in this study were calculated and are presented in Table 5. Investigations regarding PAHs sources utilized concentrations ratios of FLA/(FLA + PYR) and BaA/(BaA + CHR) in green, herbal and black tea samples as presented. Results indicate that the PAHs in the tea samples might be attributed mainly to combustion of biomass and aerial depositions from vehicular emissions. Biomass burning during the manufacturing process of tea products has been confirmed as a major contributor of PAHs (Lin and Zhu, 2004). Coal, grass and wood burning could also contribute to high PAHs contents, especially during drying at the processing stages of the plant. Tea leaves possess a large surface area that could contribute to accumulation of PAHs via aerial deposition arising from vehicular releases, during cultivation or transportation over long distances (Meharg et al., 1998). PAHs are naturally present in crude oil, engine oils, lubricating oils and coal, which may also come from machinery used in the tea plant processing.

### 3.4. Lifetime cancer incident risk assessments

The risk values, which represent the likelihood of lifetime exposure to cancer in children and adult Nigerians, are presented in Tables 6 and 7 for green, herbal, and black tea samples. According to permissible limits or acceptable risk levels defined by US EPA, the upper ($UAT_{RI}$) and lower ($LAT_{RI}$) acceptable risk thresholds are represented by one in ten thousand level ($10^{-4}$ mg/kg/day) and one in a million ($10^{-6}$ mg/kg/day) level over an average lifetime of 70 years, respectively. The $UAT_{RI}$ and $LAT_{RI}$ indicate considerable and acceptable risk levels, respectively. From the computed results, all investigated tea samples exceeded the $R_I$ permissible limits for PAHs in both children and adults. These levels may present considerable health risks to children and adults consuming these tea products. Among the green teas, this risk is highest in LGS, SBG, HGT, and TWG, indicating a cancer risk of 40.8

cases per 10000, increasing to 62.1 cases in persons under age 18. The tea products TPG and LGL indicate relatively low risk levels of 4.0 (adults) and 9.6 (under 18s) cases per 10000 people. This study reveals higher cancer risk levels in herbal and black teas. Generally, the results showed that children had higher probability of cancer risk exposure than adults.

## 4. Conclusions

PAHs in twenty-three (23) tea samples commercially sold in major superstores and markets, and widely consumed by Nigerians were successfully analysed. All the tea samples analysed showed considerably high levels of PAHs. Based on the mass distribution percentages of PAHs in the tea samples, the high molecular weight 4- and 5-membered ring PAHs dominated the green, black and herbal teas, although 2- and 3-fused ring low molecular weight PAHs were also detected. The carcinogenic BaP content in green, black and herbal tea-leaves ranged from 1.12 to 15.9, 2.04 to 6.22, and 0.76 to 28.35 µg/kg, respectively. However, the levels of ΣPAH4 (sum of benzo[a]anthracene (BaA), benzo[a]pyrene (BaP) benzo[b]fluoranthene (BbF), and chrysene (CHR)) in green, black and herbal tea leaves ranged from 1.28 to 44.57 µg/kg, and from 4.34 to 11.2 µg/kg, and from 0.76 to 34.8 µg/kg, respectively. Locally produced brands of black and herbal tea were found to contain lower concentrations of PAHs compared with some of the imported brands. The results suggest that locally produced brands were not significantly contaminated by PAHs.

## Conflicts of interest

The authors declare no conflict of interest.

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