

# Toxic metals in cigarettes and human health risk assessment associated with inhalation exposure

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Abstract This study evaluated the concentrations of cadmium (Cd), copper (Cu), iron (Fe), manganese (Mn), lead (Pb), and zinc (Zn) in 10 branded cigarettes commonly consumed in Nigeria. Chemical sequential extraction method and pseudo-total metal digestion procedure were used for extraction of metals from filler tobacco and filter samples. Samples were analyzed using flame atomic absorption spectrometry (FAAS). The filler tobacco of cigarettes had Cd, Cu, Fe, Mn, Pb, and Zn concentrations in the ranges of 5.90–7.94, 18.26-34.94, 192.61-3494.05, 44.67-297.69, 17.21-74.78, and 47.02-167.31 µg/cigarette, respectively. The minimum and maximum concentrations in the filter samples were 8.67–12.34  $\mu$ g/g of Cd, 1.77–36.48  $\mu$ g/g of Cu, 1.83–15.27 µg/g of Fe, 3.82–7.44 µg/g of Mn, 4.09-13.78 µg/g of Pb, and 30.07-46.70 µg/g of Zn. The results of this study showed that the concentrations of heavy metals in the filler tobacco samples were consistently higher than those obtained for the cigarette filters except for Cd. Toxic metals were largely found in the most labile chemical fractions. Moderate to very high risks are found associated with potential exposure to Cd and Pb. The carcinogenic risks posed by Cd and

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O. O. Ayejuyo Department of Chemistry, University of Lagos, Lagos, Nigeria Pb ranged between 1.87E-02 and 2.52E-02, 1.05E-03 and 4.76E-03, respectively, while the non-carcinogenic risk estimates for Cd and Pb were greater than 1.0 (HI > 1). Toxic metals in cigarette may have significant carcinogenic and non-carcinogenic health effects associated with inhalation exposure. Continuous monitoring and regulations of the ingredients of imported and locally produced tobacco products are advocated.

 $\label{eq:constraint} \begin{array}{l} \textbf{Keywords} \ \mbox{Tobacco} \cdot \mbox{Cigarette brands} \cdot \mbox{Heavy metals} \cdot \\ \mbox{Chemical fractionation} \cdot \mbox{Risk assessment} \end{array}$ 

# Introduction

Tobacco (Nicotiana tobacum L.) is an herbaceous plant that is commercially cultivated and processed into cigarettes. Raw tobacco leaves and cigarette smoke contain over 250 known harmful phytochemicals and metal toxicants, with at least 69 of them capable of causing cancer (USDHHS 2010a, 2014; NTP 2014). Tobacco leaves are significantly fortified with nicotine alkaloid content as its foremost component and this highly induces cigarette addiction (Armendáriz et al. 2015; Tuesta et al. 2011). Nicotine addictive effects are comparable to widely banned drug products derived from cocaine (Erythroxylum coca and E. novogranatense) and opium (Papaver somniferum) (EOL 2016). Recent report by World Health Organization estimates that globally, about 22% of people age 15 and above are cigarette smokers. The report also states that in 2011, the prevalence of cigarette smoking by female and male

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Nigerians ages 15 and over is 2 and 11%, respectively (WHO 2012). These figures are expected to increase considering enhanced local production capacity by tobacco companies in Nigeria, and increased illicit cigarette importation. Cigarette (tobacco) smoking increases risk for death and is associated with about 90 and 80% of deaths from respiratory diseases (emphysema, chronic bronchitis, and chronic obstructive thoracic disease) and lung cancer, respectively (NHS 2014). Several other cancers associated with cigarette smoking include trachea, liver, kidney, colorectal, blood, and pancreas cancers. Cigarette smoking has been reported to enhance the chances of developing heart disease, stroke, infertility, and increase risks for miscarriage and birth defects (USDHHS 2010a, 2010b, 2014, 2016). Although the health and environmental risks associated with tobacco consumption have been established, many people all over the world habitually consume tobacco without recourse to the myriad health effects including death. Worldwide, cigarette smoking is on the increase especially in low- and middle-income countries (LMCs), and tobacco-related deaths are estimated at six million per year. Based on current trends, tobacco consumption is projected to cause over eight million deaths per year in 2030, with about 4.8 million of these deaths occurring in LMCs (WHO 2011, 2013; da Costa e Silva 2015). According to reports, exposures of factory workers to particulates from raw tobacco leaves in poorly ventilated conditions have been attributed to enhanced blood pressure and aggravation of respiratory diseases (EnviroNews 2016).

Tobacco products are known to contain toxic, carcinogenic, genotoxic, and mutagenic substances (Afridi et al. 2013; Armendáriz et al. 2015; Ashraf 2012; Grant et al. 2004; Massadeh et al. 2005; Nada et al. 1999; Piadé et al. 2015; Shaikh et al. 2002; Yang et al. 2005). Among the several components in tobacco products, enhanced elemental concentrations have been reported in processed tobacco leaves, cigarette smoke, and filter (Ajab et al. 2008; Arain et al. 2008; Caruso et al. 2014; de Sousa Viana et al. 2010; Ebisike et al. 2004; Martínez et al. 2008; Massadeh et al. 2005; Pappas 2011; Pérez-Bernal et al. 2011; Vega-Carrillo et al. 1995; Zulfigar et al. 2006). Tobacco leaves possess a significant surface area and may characteristically trap heavy metals from aeolian resuspension of metal-laden dusts. The manufacturing process of cigarettes may also result in introduction of heavy metals. Heavy metal uptake by N. tabacum L. from contaminated soil particles where they are cultivated has been reported. The absorption of metals by plants and subsequently translocation and bioaccumulation in leaves at unusually high concentrations are well documented (Benson and Ebong 2005; Kelepertzis 2014; O'Connor et al. 2010; Oorts 2013; Rodríguez-Ortíz et al. 2006; Udosen et al. 2006). However, the preference for metal uptake and bioaccumulation by tobacco plant is a function of several factors namely soil type, pH, soil amendments with sewage sludge, fertilizers, and pesticides application, climatic conditions, plant variety, stalk position, and manufacturing process (Benson 2006; Chen et al. 2016; Kazi et al. 2009a; Kelepertzis 2014; Mulchi et al. 1992). Trace elements are ubiquitous and naturally occurring, while a significant percentage of soil's total metal load is largely introduced via human-mediated activities. At low concentrations, some trace metals are particularly essential as micro- and macro-nutrients, however, the non-essentiality of a large number of others is expressed by their toxic characteristics even at insignificant levels (Hartwig and Jahnke 2017; LetiniL et al. 2016; Pappas 2011). Many reports have indicated that the genotoxicity and carcinogenicity of heavy metals are primarily subject to the oxidation state of the metal species, as it directly influences their bioavailability, intracellular transport, distribution, and uptake (Annangi et al. 2016; Koedrith and Seo 2011; Stavrides 2006).

Although tobacco leaves, cigarette fillers, and filters have been recognized as sources of toxic metals that pose serious human health and environmental risks, and there are several reports conducted worldwide on different brands of cigarettes that simply quantify heavy metals as total concentration (Afridi et al. 2013; Armendáriz et al. 2015; Galázyn-Sidorczuk et al. 2008; Iwegbue et al. 2009; Kazi et al. 2009a; Nnorom et al. 2005; Shaikh et al. 2002; Verma et al. 2010; Yang et al. 2005; Pérez-Bernal et al. 2011), there is dearth of data that took into account the sequential extraction method. In recent times, growing concession by researchers indicates that trace metals quantified as total concentrations basically spotlights an oversimplified method of expressing metal contamination, without elucidating their physicochemical forms, bioavailability, and potential dispersion and remobilization within human system, and toxicity. This disposition particularly reinforces the strong advocacy for fractionation studies despite analytical uncertainties and procedural limitations (Benson et al. 2013; Pérez et al. 2008). In the environment and biosystems, heavy metal association in different geochemical fractions is principally defined by their binding strength and coupled reactivity. However, the degree of their relative stability within a specific geochemical phase determines their biological availability, potential mobility, and toxicological signatures. Generally, fractionation analysis is accepted and widely employed as a reliable analytical approach for partitioning the chemical species of elements while providing vital information about their mobility, potential risks to human health, and bioactivity (Benson et al. 2008, 2013; Kot and Namiesnik 2000; Li et al. 2015; Schleicher et al. 2011; Templeton et al. 2000). The kinetically labile metals are bound to the exchangeable fraction and are considered to possess very high bioavailability, making them more deleterious to the human system.

Sequential extraction methods basically employ chemical protocols compose of chemical reagents, apparatuses, and specific operational conditions to systematically extract elements from metal-bound phases as a means of characterizing various coexisting chemical fractions (Benson et al. 2013; Ryan et al. 2008). Several phase-selective chemical extractions procedures have been developed: the Tessier extraction technique (Tessier et al. 1979), the modified BCR (European Community Bureau of References) extraction procedure (Davidson et al. 1999; Rauret et al. 1999; Ure et al. 1993), Moćko and Wacławek three-step extraction procedure (Moćko and Wacławek 2004), Chester's sequential extraction procedure (Chester et al. 1989), multistep phase-selective extraction scheme (Nowak 1995; Jervis et al. 1995), Zatka's extraction technique (Zatka et al. 1992), and Krishnamurti's procedure (Krishnamurti et al. 1995). The present study employed a six-step fractionation procedure reported by Nowak (1995) for heavy metal association studies in branded cigarettes and filters. Although scientific reports focusing on total metal concentrations in tobacco products abound, the use of pseudo-total digestion procedure and sequential extraction method for quantifying total metal as well as fractionation concentrations is lacking, and therefore justifies the present research. The specific objectives of this study are to determine and investigate the concentrations and partitioning of heavy metals (Cd, Cu, Fe, Mn, and Pb) into geochemical fractions of cigarette matrices (filler tobacco and filters) in brands commonly sold in Nigeria, and to evaluate the probable health implications associated with exposure to these heavy metals.

# Experimental

#### Sampling and cigarettes pretreatment

Ten commercially available brands of locally manufactured cigarettes in Nigeria were randomly selected for this study. The samples were purchased at various retail outlets in Lagos and Ogun States, Southwestern Nigeria at different dates and location to account for potential variation in manufacturing dates and batches. The unopened cigarette packs were assigned identification numbers: Benson and Hedges (BAH), London Filter (LNF), London Menthol (LNM), Aspen (ASP), Pall Mall Green (PMK), Yes International (YIL), St. Moritz (SMZ), Rothmans (RTM), Pall Mall Red (PMF), and Consulate (CNS). All the cigarette brands considered in this study are products of British American Tobacco, Nigeria except ASP and YIL, which are produced by International Tobacco Company, Nigeria. Three samples of each brand of cigarette in their original packaging were individually placed in an electronic weighing balance to obtain the average weight of each brand. For representativeness, fifteen (15) sticks of cigarette per brand (5 cigarette sticks per 3 packets per brand) were cut open longitudinally, and the tobacco contents (fillers) were emptied into prewashed dried and properly marked plastic bags. Also, the filters were carefully placed in separately marked containers. Representative subsamples from composite cigarette samples were obtained using coning and quartering procedures. The analyses of the cigarette filters were carried out after smoking by volunteers. During cigarette smoking, precaution was taken to avoid sources of cross contamination by volunteers, and the smoking process was stopped once the line on the butt was reached.

## Reagents and glassware

All reagents used were of analytical grade and highest purity. HNO<sub>3</sub>, HCl, H<sub>2</sub>O<sub>2</sub>, and MgCl<sub>2</sub> were purchased from Merck (Darmstadt, Germany). Standard solutions of Cd, Cu, Fe, Mn, and Pb were prepared by stepwise dilution of certified standard stock solutions (1000  $\mu$ g mL<sup>-1</sup>) purchased from Inorganic Ventures (Christiansburg, USA). In order to maintain the quality of the analytical procedures and minimize cross contamination, all PTFE flasks and glassware were washed with detergent, pretreated by soaking in 5 M HNO<sub>3</sub> for 24 h, and rinsed thoroughly with distilled water, and later with deionized water before they were dried in the oven.

# Moisture content analysis

Empty porcelain crucibles were collected and sterilized in a muffle oven at 500 °C for 24 h prior to obtaining their individual weight. One gram of each sample was added to the crucibles and reweighed. The samples were placed in the oven at a temperature of 105 °C for 3 h. Thereafter, the samples were placed in the desiccator for 20 min, and later reweighed (after cooling) together with the crucible. The % moisture content was calculated based on the different weight measurements taken.

# Multistep heavy metal extraction procedures

Sequential extractions were carried out using a six-step phase-selective extraction scheme reported by Nowak (1995) and Jervis et al. (1995). The analytical procedure was designed to sequentially extract heavy metals into six fractions: (i) exchangeable (F1), (ii) carbonate bound (F2), (iii) Mn oxides bound (F3), (iv) Fe-Mn oxides bound (F4), (v) organic matter and sulphides-bound (F5), and (vi) residual (F6). The tobacco and filter samples of each cigarette brand were fractionated using the scheme outlined in Table 1.

Pseudo-total metal digestion procedure

The pseudo-total concentrations of metals were assessed following a microwave-assisted digestion procedure. One gram of dried, ground, and sieved filler tobacco sample was weighed and treated with 10 mL mixture of a 2:1 (v/v) HNO<sub>3</sub>—H<sub>2</sub>O<sub>2</sub> acid digest cocktail in PTFE flasks and later placed in a PTFE container. The sample-acid mix in each sealed flasks was subjected to microwave heating for 50 mins at 50% of microwave energy (800 W) and was allowed to cool and later placed on an electric hotplate and evaporated to dryness. The resulting digests were dissolved in 5 mL 1 M HNO3 and filtered through no. 4 Whatman filter paper into a 10-mL volumetric flask, and the solution adjusted to 10 mL using deionized water. Cigarette filters of each brand were subjected to same digestion procedure. Replicate analyses were carried out for each filler tobacco and filter samples in order to evaluate the reproducibility of the measurements.

# Recovery

Recoveries of heavy metals by sequential extraction method (SEM) were determined by calculating the ratio of the total concentrations of metals in F1, F2, F3, F4, F5, and F6 fractions and the pseudo-total metal levels. The recovery of SEM used in this

Table 1 Details of the sequential extraction scheme, analytical reagents, and apparatus

Fraction	Extraction procedure
F1 - Exchangeable	1.0 g of dried, ground, and sieved tobacco sample was extracted with 20 mL MgCl <sub>2</sub> (1.0 mol/dm <sup>3</sup> ) (pH $^{7}$ ) + continuous agitation for 60 mins.
F2 - Carbonate bound	Tobacco residue from fraction 1 (F1) was leached with 20 mL NaOAc (1.0 mol/dm <sup>3</sup> ) (pH 5) (adjusted using acetic acid) + continuous agitation for 5 h.
F3 - Mn oxides bound	Residue obtained from fraction 2 (F2) was extracted with 20 mL NH <sub>4</sub> OH.HCl (0.1 mol/dm <sup>3</sup> ) in HNO <sub>3</sub> (0.01 mol/dm <sup>3</sup> ) for 60 mins at room temperature with occasional agitation.
F4 - Fe-Mn oxides bound	Tobacco residue from fraction 3 (F3) was leached with 20 mL of $NH_4OH.HCl (0.04 mol/dm^3)$ in $CH_3COOH (4.4 mol/dm^3)$ for 8 h at 98 °C with occasional agitation.
F5 - Organic matter and sul- phides bound	Cigarette residue in fraction 4 (F4) was extracted with 20 mL 30% $H_2O_2$ solution (pH adjusted 2 with HNO <sub>3</sub> ) (0.02 mol/dm <sup>3</sup> ) and later placed in water bath for 5 h at 85 °C with intermittent manual agitation. On cooling, 5.0 mL NH <sub>4</sub> OAc (3.2 mol/dm <sup>3</sup> ) and 20% ( $\nu/\nu$ ) HNO <sub>3</sub> was added. The mixture was diluted with 10.0 mL 20% $H_2O_2$ with continuous agitation for 60 min.
F6 - Residual	To bacco residue from fraction 5 (F5) was extracted in a Teflon vessel with 50 mL of 40% HF and 10 mL of 60% HClO <sub>4</sub> acid.

study was mathematically computed as shown below:

$$Recovery\% = \begin{bmatrix} \sum_{i=1}^{n} F_i \\ C_{Total} \end{bmatrix} \times 100$$
(1)  
$$\sum_{i=1}^{n} F_i = F1 + F2 + F3 + F4 + F5 + F6$$

where  $F_i$  is the sum of concentrations of heavy metals extracted in F1, F2, F3, F4, F5, and F6, and  $C_{Total}$  is the pseudo-total metal concentration. The recoveries of the SEM to the pseudo-total procedure were satisfactory and ranged from 96.81–101.71% for Cd, 96.21– 104.10% for Cu, 93.79–106.02% for Fe, 98.29– 103.32% for Mn, 98.91–104.80% for Pb, and 97.01– 100.36% for Zn, respectively. Comparatively speaking, the calculated recoveries indicate that the heavy metal concentrations derived from addition of the values for respective chemical fractions are consistent with concentrations determined from pseudo-total metal digestion procedure. This implies that this sequential extraction method employed for this work is reliable and reproducible.

#### Instrumentation

Electric oven (Genlab thermal oven Model MIN0175, UK) was used for drying tobacco and filter samples. Glass mortar and pestle (model HG24-080) was used for grinding the dried filler tobacco samples. The concentrations of Cd, Cu, Fe, Mn, Pb, and Zn in each extract from filler and filter samples were determined using S Series S4 AA System flame atomic absorption spectrometer (FAAS) (Thermo Electron Corporation, UK). Table 2 shows the analytical lines for each heavy metal, as well as the spectrometer and flame operating conditions.

#### Human health risk assessment

The heavy metals considered in the present study are classified either as non-carcinogenic or carcinogenic metals. According to the Integrated Risk Information System (IRIS), copper (Cu), iron (Fe), manganese (Mn), and zinc (Zn) are classified as non-carcinogenic metals. However, the carcinogenic metals investigated in this

Table 2Spectrometer and flame parameters for FAAS (S Series S4)

54)		
RF frequency	185–760 nm	
Measurement mode	Absorbance	
Signal type	Continuous	
Operating power	300VA	
Sample flow rate	1.0 L/min	
Burner type	Titanium	
Burner height	7.0 mm	
Nebulizer type	PE Tube	
Nebulizer uptake	4.0 s	
Flame type	Air-C <sub>2</sub> H <sub>2</sub>	
Stabilization time	0 mins	
Fuel flow	1.0-1.2 L/min	
Absorption wavelengths and b	bandpass (nm) for	metals
	$\lambda$	Bandpass
Cadmium	228.8	0.2
Copper	324.8	0.2
Iron	248.3	0.2
Manganese	279.5	0.2
Lead	219.0	0.5
Zinc	213.9	0.2

study included cadmium, Cd (group B1) and lead, Pb (group B2), known as probable human carcinogens. Health risk estimation considered two categories of heavy metals which could potentially induce long-term effects: (a) carcinogenic metals (Cd, Pb), and (b) noncarcinogenic (Cd, Cu, Mn, Pb, Zn). The purpose for conducting the toxicity assessment is to check the likelihood that toxic metals present in cigarette filler upon emission during smoking could pose serious health effects to the smokers and non-smokers through direct inhalation exposure. The human health exposure assessment and risk characterization associated with noncarcinogenic and carcinogenic heavy metals were calculated using US EPA's methodology (https://www.epa. gov/expobox/exposure-assessment-tools-routesinhalation) as expressed in Eqs. (2) and (3). The incremental life cancer rate (ILCR) and hazard index were estimated according to Eqs. (4) and (5) below. In this estimation, we have assumed that the heavy metals present in cigarette filler will be emitted and transferred in the mainstream smoke during cigarette smoking and would be deposited into the human respiratory system through inhalation.

$$C_{c-adj-nc} = \frac{C_c \times ET \times EF \times ED \times CF}{AT}$$
(2)

$$C_{c-adj-c} = \frac{C_c \times ET \times EF \times ED \times CF}{AT \times LT}$$
(3)

where  $C_c$  is the concentration of non-carcinogenic and carcinogenic metal from cigarette ( $\mu g/g$ ), ET is the exposure time (6 h/day), EF is the frequency of the exposure (250 days/year), ED is the duration of exposure (30 years), AT is the averaging time (days; ED × 365 days/year), CF is the conversion factor (day/24 h) (4.2E-02), and LT is the lifetime (70 years). According to EPA, for carcinogens, the concentration is averaged over the lifetime of the exposed individual (often assumed to be 70 years) (USEPA 2009, 2011).

$$ILCR = IUR \times LADD_a \tag{4}$$

$$HI = LADD_c/RfC \times 1000\mu g/g \tag{5}$$

where ILCR is the incremental lifetime cancer rate, IUR is the inhalation unit risk (per mg/m<sup>3</sup>), and LADD is the lifetime average daily dose. According to EPA, the IUR for Cd and Pb are  $1.8 \times 10^{-3}$  and  $8.0 \times 10^{-5}$  per  $\mu$ g/m<sup>3</sup>. respectively. The hazard index (HI) estimated for noncarcinogenic risk using inhalation reference concentration (RfC) indicates non-cancer health risks that might be associated with potential inhalation exposure of the metals to smokers over a lifetime (USEPA 1994). Based on US EPA's assessment, total cancer risks associated with exposure to contaminants over a lifetime greater than 1.00E-6 are generally considered unacceptable (USEPA 1991). Generally, the US EPA's threshold range indicated for tolerable risk is between 1.00E-4 and 1.00E-6 (i.e., the probability of 1 in 10,000 to 1 in 1000,000 that an individual may develop cancer from lifetime exposure to a carcinogen) as a commonly referenced benchmark for the protection of public health (Behera et al. 2014; Benson et al. 2016). However, for non-cancer risk characterization, HI greater than 1 indicates there is a potential for adverse health effects. On the other hand, if HI < 1, this suggests that it is unlikely for a smoker to have non-carcinogenic health effects.

## **Results and discussion**

#### Manufacturers' information

Preliminary assessments of weighed cigarette brands with their respective tar, nicotine, and carbon monoxide contents as reported on individual packs are shown in Table 3. A classification of cigarette brands based on nicotine content was done. According to conventional guidelines, if the nicotine levels  $\leq 0.6$  mg, the cigarette is considered to be light; otherwise, it is ranked as normal. Cigarette brands used in this study were all classified as normal.

Moisture contents in filler tobacco and filter samples

The percentage moisture contents in the investigated cigarette samples are presented in Table 4. Results indicate that the tobacco and filter samples showed similar percentages among all the cigarette brands analyzed. However, BAH (Benson & Hedges®) cigarette filler had the highest moisture content of 14.75% while PMF (Pall Mall Filter®) cigarette had the lowest moisture of 12.77%. For the cigarette filters, CNS (Consulate®) and ASP (Aspen®) cigarettes indicated the highest and lowest percent moisture contents, respectively.

#### Metals in different components of cigarettes

The chemical fractionation and pseudo-total metal concentration results of the Cd, Cu, Fe, Pb, Mn, and Zn per brand of filler tobacco are presented in Table 5. The concentrations of heavy metals in geochemical fractions (F1-F6) of filter samples of cigarette brands are presented in Fig. 1. Generally, the results indicated significant differences in the concentration of heavy metals in both the filler tobacco and the filter samples. The minimum and maximum concentrations in filler tobacco samples ranged between 5.90 and 7.94 µg/g of Cd, 18.26 and 34.94 µg/g of Cu, 192.61 and 3494.05 µg/g of Fe, 44.67 and 297.69  $\mu$ g/g of Mn, 17.21 and 74.78  $\mu$ g/g of Pb, and 47.02 and 167.31  $\mu$ g/g of Zn (Table 5). On the other hand, the values measured in the filter samples varied from 8.67–12.34 µg/g of Cd, 1.77–36.48 µg/g of Cu, 1.83-15.27 µg/g of Fe, 3.82-7.44 µg/g of Mn, 4.09-13.78 µg/g of Pb, and 30.07–46.70 µg/g of Zn (Fig. 1). The highest concentration of Cd, Cu, Fe, Mn, Pb, and Zn metals was found in St. Moritz<sup>®</sup>, Yes International<sup>®</sup>,

Brand	Manufacturer	Code	Weight (mg)	Nicotine (mg)	Tar content (mg)	CO (mg)	Classification (light or normal)
Benson & Hedges	British American Tobacco	BAH	25.35	1	10	10	Normal
London Filter	British American Tobacco	LNF	24.38	0.8	12	10	Normal
London Menthol	British American Tobacco	LNM	24.21	1	10	10	Normal
Aspen	International Tobacco Company	ASP	24.46	0.8	10	10	Normal
Pall Mall (Green)	British American Tobacco	PMK	24.43	0.8	12	10	Normal
Yes International	International Tobacco Company	YIL	26.59	1.1	12	9	Normal
St. Moritz	British American Tobacco	SMZ	29.70	1	10	10	Normal
Rothmans	British American Tobacco	RTM	23.94	1	10	10	Normal
Pall Mall (Red)	British American Tobacco	PMF	24.41	0.8	12	10	Normal
Consulate	British American Tobacco	CNS	14.34	1	12	10	Normal

Table 3 Nicotine, tar and carbon monoxide composition according to the manufacturer

BAH Benson and Hedges, LNF London Filter, LNM London Menthol, ASP Aspen, PMK Pall Mall Krystal Blast, YIL Yes International, SMZ St. Moritz, RTM Rothmans, PMF Pall Mall Filter, CNS Consulate

London Filter®, Aspen®, and London Menthol®, respectively. It was observed that the concentrations of heavy metals in the filler tobacco samples were consistently higher than those obtained for the cigarette filters except for Cd. The heavy metals under investigation were not detected in the cigarette filters prior to smoking.

The Cd concentrations in the cigarette filters after smoking were found to be relatively higher than the contents in the filler tobacco, implying that enhanced level of Cd was absorbed and retained by the filters. Similar finding has been reported by Afridi et al. (2013). The maximum and minimum concentrations of Cd in cigarette filters investigated in this study were found in Yes International® and Benson and Hedges®, respectively. It was, however, observed that there was no

Table 4 Percentage moisture in tobacco and filter samples

Sample	% moisture (filler)	% moisture (filter)
BAH	14.75	5.97
LNF	13.98	5.93
LNM	14.32	5.49
ASP	14.38	5.26
РМК	13.10	5.77
YIL	12.47	6.04
SMZ	13.05	5.40
RTM	13.32	5.50
PMF	12.77	5.65
CNS	13.05	6.12

significant difference in the concentrations of Cd in the filler tobacco of the different investigated brands. A comparison of the levels of Cd in cigarette fillers investigated with brands from Spain (0.18  $\mu$ g/g), Ireland (1.73–2.02 µg/g), Canada (2.01 µg/g), USA (0.98 µg/ g), India (0.9  $\mu$ g/g), and Pakistan (1.66–2.96  $\mu$ g/g) showed the concentration of Cd are 37.77, 3.62, 3.38, 6.94, 7.55, and 2.94 times greater than results reported for cigarettes from Spain, Ireland, Canada, USA, India, and Pakistan, respectively (Armendáriz et al. 2015; Afridi et al. 1987, Wu et al. 1997; Kazi et al. 2009b). The concentrations of Cd in all the investigated brands of locally produced cigarettes were relatively higher than any of the tobacco brands commercially sold in other developed and developing countries (Table 6). Cd concentration in locally manufactured cigarettes in Nigeria earlier reported by Ebisike et al. (2004) and Nnrom et al. (2005) was found to be lower than the average fractionation concentrations reported in this present work. The enhanced concentrations of these toxic metals in the cigarette products could have been associated with factors such as the manufacturing process, fertilizer application during cultivation, and aeolian depositional processes. In addition, the extraction and fractionation procedure considered for the pretreatment of cigarette samples and analysis offered a better and reliable approach rather than total elemental quantification (Benson et al. 2013).

The concentration of Pb in the 10 branded cigarette tobacco samples ranged from 17.21 (Yes International®) to 74.78  $\mu$ g/g (London Menthol®), with an

BAH Exch Carb Mn C Fe-Mn C Pseu Pseu Resid Pseu Reco Carb Mn C Fe-Mn C														
		Mn	Zn	Pb	Cd	Cu	Fe		Mn	Zn	Ъb	Cd	Cu	Fe
	Exchangeable	14.632	22.328	7.68	1.21	2.296	2.712	ΥП	114.44	17.28	ND	1.416	8.44	25.44
	Carbonate bound	14.92	13.32	3.34	0.45	1.19	6.99		20.9	8.98	0.65	0.45	1.47	3.11
	Mn oxide bound	6.81	63.92	0.53	2.00	0.91	3.52		7.16	3.22	0.36	1.77	1.02	2.83
	Fe-Mn oxide bound	6.94	14.13	ND	0.86	5.52	864.72		7.22	2.38	ND	0.74	5.09	49.85
	Organic-sulphide bound	1.37	7.60	5.20	0.70	6.33	37.06		2.02	13.86	3.07	0.58	15.05	43.34
	Residual	ND	33.13	12.60	0.86	2.95	118.09		1.12	36.81	13.13	2.35	3.87	2039.8
	Total fractions	44.67	154.43	29.35	6.08	19.19	1033.09		152.86	82.53	17.21	7.31	34.94	2164.37
	Pseudo-total	44.75	155.02	28.62	6.14	18.44	1101.42		153.04	82.23	17.16	7.45	34.88	2157.18
	Recovery %	99.83	99.62	102.55	99.02	104.09	93.79		99.88	100.36	100.29	98.07	100.17	100.33
Exch Carb Mn ( Fe-M Orga Resi								SMZ						
Carb Mn ( Fe-N Orga Resi	Exchangeable	19.95	3.80	12.70	1.18	ND	5.88		69.33	11.125	ND	2.268	6.55	10.43
Mn c Fe-h Orga Resi	Carbonate bound	0.93	9.32	0.52	0.56	0.72	4.88		12.40	8.32	1.50	0.49	0.89	5.91
Fe-N Orga Resi	Mn oxide bound	11.92	43.22	1.40	1.90	1.34	3.81		6.09	3.22	0.92	1.72	1.47	3.72
Orga Resi	Fe-Mn oxide bound	11.76	8.67	1.47	0.85	4.83	937.64		4.92	1.37	1.65	0.77	5.08	44.46
Resi	Organic-sulphide bound	2.42	15.35	6.83	0.65	9.92	63.64		0.63	10.06	0.41	0.62	17.75	23.6
	Residual	1.27	31.30	10.83	1.85	3.10	2478.2		0.94	36.33	16.88	2.07	3.06	128.11
Tota	Total fractions	48.25	111.66	33.754	6.99	19.91	3494.05		94.31	70.425	21.36	7.94	34.80	216.23
Pseu	Pseudo-total	46.70	115.10	32.43	7.22	19.28	3503.44		94.21	71.03	21.22	7.98	35.54	216.99
Recc	Recovery %	103.32	97.01	104.08	96.81	103.27	99.73		100.11	99.15	100.66	99.47	97.92	99.65
LNM								RTM						
Excl	Exchangeable	98.25	10.95	52.2	0.36	6.38	15.75		108.19	22.9658	2.7456	1.576	14.84	15.07
Carb	Carbonate bound	6.59	65.88	1.05	0.54	0.80	7.78		18.80	11.70	0.80	0.55	1.55	5.25
Mn (	Mn oxide bound	10.30	42.00	0.61	2.10	1.23	4.83		9.22	4.50	0.72	2.02	1.55	2.92
Fe-N	Fe-Mn oxide bound	9.34	6.82	1.87	0.74	1.23	922.00		8.08	12.36	1.11	0.66	6.83	67.46
Orga	Organic-sulphide bound	1.92	11.03	5.16	0.75	10.54	41.86		2.19	11.55	4.36	0.56	4.78	41.8
Resi	Residual	0.95	30.63	13.89	2.1	2.57	2270.8		ND	28.03	11.03	2.13	2.72	120.43
Tota	Total fractions	127.35	167.31	74.78	6:59	22.75	3263.02		146.48	91.11	20.77	7.49	32.27	252.93
Pseu	Pseudo-total	127.05	169.26	73.51	6.64	22.8	3198.73		149.02	90.94	20.86	7.37	32.34	238.57
	Recovery %	100.24	98.85	101.73	99.31	99.78	102.01		98.29	100.18	99.55	101.71	99.78	106.02
ASP								PMF						
Excl	Exchangeable	128.8	23.89	1.95	0.45	4.57	11.79		50.59	9.37	2.1978	0.382	8.75	10.08
Carb	Carbonate bound	151.12	12.64	1.60	0.58	1.48	4.33		12.36	8.02	1.60	1.86	1.47	6.30

(continued)
5
Table

		Mn	Zn	Pb	Cd	Cu	Fe	Mn		Zn	Pb	Cd	Cu	Fe
	Mn oxide bound	8.52	5.87	ND	1.92	1.28	2.85	6.81	_	3.58	1.43	1.79	1.46	4.84
	Fe-Mn oxide bound	7.24	9.80	ND	0.68	5.36	50.53	5.90	0	10.96	1.53	0.78	5.30	62.04
	Organic-sulphide bound	1.74	10.09	2.50	0.74	10.97	21.14	0.68	~	9.47	3.58	0.57	2.64	30.12
	Residual	0.27	5.81	14.31	1.93	3.89	101.97	1.01	_	5.62	10.01	1.74	4.56	144.28
	Total fractions	297.69	68.097	20.36	6.29	27.55	192.61	77.35	35	47.02	20.35	7.12	24.18	257.66
	Pseudo-total	298.88	68.72	19.43	6.30	27.27	193.28	77.6	6	46.95	20.38	6.99	24.22	258.02
	Recovery %	09.60	60.66	104.80	79.97	101.03	99.65	99.68	58 ]	00.15	99.84	101.89	99.83	99.86
PMK								CNS						
	Exchangeable	70.41	11.35	Ŋ	0.36	6.78	25.44	116	116.02	16.5612	6.02	0.398	5.11	23.18
	Carbonate bound	15.77	10.26	3.22	0.45	1.94	4.69	13.11	11	9.20	0.11	0.46	1.17	2.65
	Mn oxide bound	8.11	3.73	0.35	1.98	1.60	4.04	6.40	0	2.90	0.48	1.75	1.46	2.40
	Fe-Mn oxide bound	6.57	6.48	2.01	0.68	6.17	33.98	6.43	~	13.38	1.30	0.74	5.78	35.30
	Organic-sulphide bound	2.25	10.70	5.34	0.59	13.59	33.98	1.11	_	24.98	1.89	0.79	2.34	21.28
	Residual	0.97	34.15	15.28	1.84	3.64	188.18	ND		30.24	16.84	2.12	2.40	133.00
	Total fractions	104.08	76.67	26.2	5.90	33.72	290.31	143	143.07	97.2612	26.64	6.26	18.26	217.81
	Pseudo-total	103.66	76.99	26.49	6.01	32.95	291.04	144.11	.11	97.42	25.98	6.33	18.98	218.46
	Recovery %	100.41	99.59	98.91	98.24	102.34	99.75	99.28	28	99.84	102.54	98.86	96.21	99.70
BAH B Filter, C	BAH Benson and Hedges, LNF London Filter, LNM London Menthol, ASP Aspen, PMK Pall Mall Krystal Blast, YL Yes International, SMZ St. Moritz, RTM Rothmans, PMF Pall Mall Filter, CNS Consulate	don Filter,	<i>LNM</i> Londc	m Menthol,	ASP Aspe	n, <i>PMK</i> Pa	ll Mall Krystal	Blast, YIL Ye	s Interna	tional, <i>SM</i> Z	z St. Moritz	, RTM Roth	mans, PMF	Pall Mall

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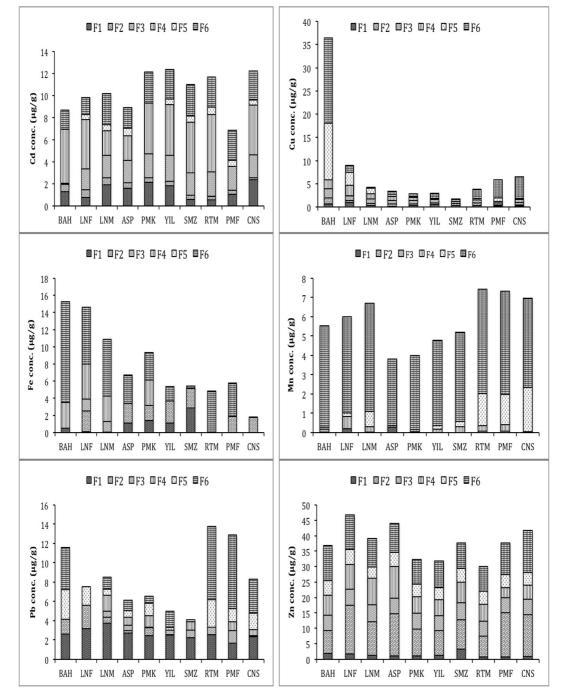


Fig. 1 Heavy metals in geochemical fractions (F1–F6) of filter samples (BAH Benson and Hedges, LNF London Filter, LNM London Menthol, ASP Aspen, PMK Pall Mall Krystal Blast, YIL

Yes International, SMZ St. Moritz, RTM Rothmans, PMF Pall Mall Filter, CNS Consulate)

average Pb level of 29.08  $\mu$ g/cigarette. Results indicate higher concentrations of Pb in cigarette tobacco than the filter samples. Comparatively speaking, the average concentration of Pb obtained for the investigated

cigarette brands was relatively higher than results found in reported literatures (Table 6). However, previous studies on heavy metal load in cigarettes commercially sold in Nigeria did not report the Pb content (Nnorom

Cd	Cu	Cr	Fe	Mn	Ni	Pb	V	Zn	Country	Reference
2.32	NR	NR	NR	NR	NR	NR	NR	NR	Austria	Kalcher et al. 1988
0.18	4.13	NR	NR	NR	2.23	0.64	NR	NR	China	Yang et al. 2005
0.65	Nd	1.43	Nd	Nd	1.26	0.27	Nd	PN	Brazil	de Sousa Viana et al. 2010
2.01	NR	NR	NR	NR	NR	NR	NR	NR	Canada	Watanabe et al. 1987
NR	NR	0.08-6.29	2864-7859	NR	NR	NR	NR	76.8–190	Egypt	Nada et al. 1999
1.7	15.6	NR	500	NR	NR	2.4	NR	50	Finland	Mussalo-Rauhamaa et al. 1986
1.95	9.70	1.11	581	NR	2.4	1.2	NR	49.8	Germany	Schneider and Krivan 1993
1.89	NR	NR	NR	NR	5.40	1.17	NR	57.6	Hungary	Gondola and Kadar 1995
0.45	14	4.07	664	NR	8.79	1.94	NR	27	India	Verma et al. 2010
0.9	39	5.0	995	NR	3.0	4.3	NR	39.5	India	Shaikh et al. 2002
1.73-2.02	Nd	PN	Nd	PN	0.72 - 1.52	0.38-1.16	Nd	PN	Ireland	Afridi et al. 2013
0.58	NR	NR	NR	NR	NR	7.39	NR	NR	Italy	Venditti 1989
1.3	NR	0.7 - 1.85	NR	76–395	NR	NR	0.8 - 3.7	33-84	Jamaica	Grant et al. 2004
1.98	NR	NR	NR	NR	NR	NR	NR	NR	Japan	Elinder et al. 1983
2.64	12.90	NR	NR	NR	NR	2.67	NR	55.62	Jordan	Massadeh et al. 2005
1.02	NR	NR	NR	NR	NR	NR	NR	NR	Korea	Jung et al., 1998
0.18-3.07	NR	0.15 - 0.49	NR	108-244.26	NR	NR	0.281-1.52	32.30-72.0	Mexico	Martínez et al. 2008
ND	NR	1.37	NR	ND	NR	NR	ND	24-65	Mexico	Vega-Carrillo et al. 1995
0.68 - 1.17	NR	NR	NR	NR	NR	NR	NR	NR	Nigeria	Ebisike et al. 2004
0.7–2.3	NR	NR	NR	NR	NR	NR	NR	NR	Nigeria	Nnorom et al. 2005
1.66–2.96	NR	NR	NR	NR	0.962 - 1.34	0.399 - 1.39	NR	NR	Pakistan	Kazi et al. 2009b
1.0-3.2	9.0-16.3	1.1 - 16.4	Nd	Nd	0.1 - 3.2	1.1 - 28.3	Nd	1.1 - 41.4	Pakistan	Zulfīqar et al. 2006
0.50	7.89	NR	NR	45.03	NR	14.39	NR	8.57	Pakistan	Ajab et al. 2008
0.61	NR	NR	NR	NR	NR	0.56	NR	NR	Poland	Galázyn-Sidorczuk et al. 2008
NR	145-267	NR	42,855–8366	1741–3748	NR	NR	NR	385-947	Spain	Pérez-Bernal et al. 2011
0.18	NR	1.442	NR	112.026	2.238	0.602	NR	NR	Spain	Armendáriz et al. 2015
1.7	2.45	1.63	NR	NR	0.22	1.02	NR	NR	Turkey	Barlas et al. 2001
0.98	NR	NR	NR	NR	NR	NR	NR	35.1	NSA	Wu et al. 1997
5.90-7.94	18.26 - 34.94	PN	192.61-3494.05	44.67–297.69	Nd	17.21–74.78	PN	47.02–167.31	Nigeria	This study

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 Table 7
 Estimated non-cancer and cancer risks of metals due to inhalation exposure to cigarettes

Sample	Metal	C <sub>c-adj-nc</sub> (mg/m <sup>3</sup> )	$C_{c\text{-}adj\text{-}c}~(mg\!/\!m^3)$	ADD <sub>a</sub> (mg/kg-day)	LADD <sub>a</sub> (mg/kg-day)	HI	ILCR
BAH	Cu	3.29E + 00	1.41E + 00	1.13E + 00	4.83E-01	1.20E-02	
	Mn	7.65E + 00	3.28E + 00	2.62E + 00	1.12E + 00	8.00E-01	
	Zn	2.64E + 01	1.13E + 01	9.07E + 00	3.89E + 00	1.30E-02	
	Cd	1.04E + 00	4.46E-01	3.57E-01	1.53E-01	7.65E + 00	1.93 E-02
	Pb	5.03E + 00	2.15E + 00	1.72E + 00	7.38E-01	4.92E + 00	4.13 E-0.
	Cu	3.41E + 00	1.46E + 00	1.17E + 00	5.01E-01	1.25E-02	
	Mn	8.26E + 00	3.54E + 00	2.83E + 00	1.21E + 00	8.64E-02	
LNF	Zn	1.91E + 01	8.19E + 00	6.56E + 00	2.81E + 00	9.37E-03	
	Cd	1.20E + 00	5.13E-01	4.10E-01	1.76E-01	8.80E + 00	2.21 E-02
	Pb	5.78E + 00	2.48E + 00	1.98E + 00	8.49E-01	5.66E + 00	4.76 E-0.
	Cu	3.90E + 00	1.67E + 00	1.34E + 00	5.72E-01	1.43E-02	
	Mn	2.18E + 01	9.35E + 00	7.48E + 00	3.20E + 00	2.29E-01	
LNM	Zn	2.86E + 01	1.23E + 01	9.82E + 00	4.21E + 00	1.40E-02	
	Cd	1.13E + 00	4.84E-01	3.87E-01	1.66E-01	8.30E + 00	2.09 E-02
	Pb	1.28E + 01	5.49E + 00	4.39E + 00	1.88E + 00	1.25E + 01	1.05 E-0.
	Cu	4.72E + 00	2.02E + 00	1.62E + 00	6.93E-01	1.73E-02	
	Mn	5.10E + 01	2.18E + 01	1.75E + 01	7.49E + 00	5.35E-01	
ASP	Zn	1.17E + 01	5.00E + 00	4.00E + 00	1.71E + 00	5.70E-03	
	Cd	1.08E + 00	4.62E-01	3.70E-01	1.58E-01	7.90E + 00	1.99 E-02
	Pb	3.49E + 00	1.49E + 00	1.20E + 00	5.12E-01	3.41E + 00	2.87 E-0
	Cu	5.77E + 00	2.47E + 00	1.98E + 00	8.48E-01	2.12E-02	
	Mn	1.78E + 01	7.64E + 00	6.11E + 00	2.62E + 00	1.87E-01	
PMK	Zn	1.31E + 01	5.63E + 00	4.50E + 00	1.93E + 00	6.43E-03	
	Cd	1.01E + 00	4.33E-01	3.46E-01	1.48E-01	7.40E + 00	1.87 E-02
	Pb	4.49E + 00	1.92E + 00	1.54E + 00	6.59E-01	4.39E + 00	3.69 E-0
	Cu	5.98E + 00	2.56E + 00	2.05E + 00	8.79E-01	2.20E-02	
	Mn	2.62E + 01	1.12E + 01	8.97E + 00	3.85E + 00	2.75E-01	
YIL	Zn	1.41E + 01	6.06E + 00	4.85E + 00	2.08E + 00	6.93E-03	
	Cd	1.25E + 00	5.36E-01	4.29E-01	1.84E-01	9.20E + 00	2.31 E-02
	Pb	2.95E + 00	1.26E + 00	1.01E + 00	4.33E-01	2.89E + 00	2.42 E-0.
	Cu	5.96E + 00	2.55E + 00	2.04E + 00	8.76E-01	2.19E-02	
	Mn	1.61E + 01	6.92E + 00	5.54E + 00	2.37E + 00	1.69E-01	
SMZ	Zn	1.21E + 01	5.17E + 00	4.13E + 00	1.77E + 00	5.90E-03	
	Cd	1.36E + 00	5.83E-01	4.66E-01	2.00E-01	1.00E + 01	2.52 E-02
	Pb	3.66E + 00	1.57E + 00	1.25E + 00	5.37E-01	3.58E + 00	3.00 E-0.
	Cu	5.53E + 00	2.37E + 00	1.89E + 00	8.12E-01	2.03E-02	
	Mn	2.51E + 01	1.07E + 01	8.60E + 00	3.69E + 00	2.63E-01	
RTM	Zn	1.56E + 01	6.69E + 00	5.35E + 00	2.29E + 00	7.63E-03	
	Cd	1.28E + 00	5.50E-01	4.40E-01	1.89E-01	9.45E + 00	2.38 E-02
	Pb	3.56E + 00	1.52E + 00	1.22E + 00	5.23E-01	3.49E + 00	2.92 E-03
	Cu	4.14E + 00	1.77E + 00	1.42E + 00	6.08E-01	1.52E-02	
	Mn	1.32E + 01	5.68E + 00	4.54E + 00	1.95E + 00	1.39E-01	
PMF	Zn	8.05E + 00	3.45E + 00	2.76E + 00	1.18E + 00	3.93E-03	
	Cd	1.22E + 00	5.23E-01	4.18E-01	1.79E-01	8.95E + 00	2.26 E-02

Sample	Metal	C <sub>c-adj-nc</sub> (mg/m <sup>3</sup> )	$C_{c-adj-c} (mg/m^3)$	ADD <sub>a</sub> (mg/kg-day)	LADD <sub>a</sub> (mg/kg-day)	HI	ILCR
	Pb	3.48E + 00	1.49E + 00	1.19E + 00	5.12E-01	3.41E + 00	2.87 E-03
	Cu	3.13E + 00	1.34E + 00	1.07E + 00	4.59E-01	1.15E-02	
	Mn	2.45E + 01	1.05E + 01	8.40E + 00	3.60E + 00	2.57E-01	
CNS	Zn	1.67E + 01	7.14E + 00	5.71E + 00	2.45E + 00	8.17E-03	1.98 E-02
	Cd	1.07E + 00	4.59E-01	3.68E-01	1.58E-01	7.90E + 00	3.75 E-03
	Pb	4.56E + 00	1.95E + 00	1.56E + 00	6.70E-01	4.47E + 00	

Table 7 (continued)

et al. 2005; Ebisike et al. 2004). The average Pb concentration in ten cigarette brands under study indicates metal loads that are 6.76, 3.94, 1.89, and 2.02 times higher than those cigarette tobacco brands sold in India, Italy, Jordan, and Pakistan, respectively. Potentially toxic metals such as Cd and Pb have been linked with cigarette smoking-related physiological disorders such as cardiovascular and pulmonary diseases in humans primarily through inhalation pathway (Fitzpatrick and Blair 2000; Kazi et al. 2008, Afridi et al. 2013). Peripheral arterial diseases, interference with hemostasis, and hypertension are possible health effects that have been linked to Pb exposure through active and passive smoking in adults and children (Ding et al. 2000, Mannino et al. 2003, Navas-Acien et al. 2004). As a result of these high levels of Cd and Pb in the investigated cigarette brands, locally produced and widely consumed by a significant proportion of the Nigeria population, there would be increased concerns about possible exposure to these toxic metals during cigarette smoking.

## Human health risk assessment

Table 7 shows the estimated non-carcinogenic and carcinogenic risks of metals that may be associated with direct inhalation exposure to cigarettes by a typical smoker. The human cancer risks posed by Cd and Pb ranged between 1.87E-02 and 2.52E-02, 1.05E-03 and 4.76E-03, respectively. Notably, the potential carcinogenic risk estimated for Cd was generally higher than Pb. The incremental lifetime cancer rate values for Cd and Pb for all cigarettes investigated were above the acceptable limit (1.00E-4) stipulated by US EPA. In other words, the chances of developing experiencing cancer during the lifetime of an active smoker through inhalation exposure of Cd-laden smoke could be 252 in

10,000 cases, while the likelihood of getting cancer via Pb was estimated to be 47.6 cases in 10, 000 cases. This implies that carcinogenic risk through inhalation exposure among active cigarette smokers is likely on the long term. The non-carcinogenic health risk associated with inhalation exposure to Cu, Mn, Zn, Cd, and Pb was estimated on the basis of the concentration of toxic metals present in fractions of cigarette filler. It was observed that the hazard index for Cu, Mn, and Zn were generally less than 1.0 for all the cigarettes investigated (Table 7). However, the non-carcinogenic risk estimates for Cd and Pb were greater than 1.0 (HI > 1). The present study shows that the estimated HI for Cd was higher compared to Pb except in LNM, and varied from 7.65 in BAH to 10.0 in SMZ. The non-cancer risk, HI, for Pb ranged between 2.89 and 12.5 in YIL and LNM samples, respectively. Therefore, it can be inferred that having HI estimates greater than 1.0 indicate that Cd and Pb concentrations could pose non-cancer health effects to the smokers through direct and long-term inhalation exposure.

Results obtained from the sequential extraction (fractionation) method of heavy metals in cigarette filler and filter samples are presented in Table 5 and Fig. 1, respectively. The sequential fractionation procedure revealed significant labile fractions (exchangeable + carbonate bound) particularly for the most toxic Cd and Pb metals in both the filler tobacco and filter samples of most brands. The sum of these two most labile fractions showed significant concentrations of Mn, Zn, and Cu in both the filler and filter samples. Moderate to very high risks may be associated with potential exposure to Cd and Pb in 95% of understudied brands of filler tobacco and filters. The total concentration of metals in any matrix provides an exaggerated estimation of their occurrence and pollution and do not largely reflect on their degree of contamination as well as envisage metalassociated risks to living systems. Heavy metals in the most labile fractions are known to be unstable and weakly bound to an environmental matrix (Benson et al. 2013, 2016; Tessier et al. 2011), and their bioavailability and toxicity is a function of their chemical fractionation (Yuan et al. 2015, Benson et al. 2016). According to the chemical fractionation results, Cd and Pb representing the most toxic metals in the present study showed high bioavailability and could be readily transferred and bioaccumulated in the blood, lungs, liver, and kidney during cigarette smoking (Afridi et al. 2012; Csalari and Szantai 2002). The pseudo-total and fractionation concentrations of Cd and Pb in all filler tobacco and filter samples were equally high, indicating that their toxicities and bioavailabilities during possible exposure might be enhanced by their existing chemical fractions. The combustion of cigarette is known to produce cadmium oxide, which is highly bioavailable with about 30-40% absorbed and circulated during exposure via inhalation of cigarette smoke (Arain et al. 2008).

## Conclusions

This study provides a novel insight into the occurrence, concentration, and risk assessment associated with exposure to Cd, Cu, Fe, Pb, and Zn in locally manufactured cigarette brands commonly sold and consumed in Nigeria. The results of heavy metal concentrations revealed that filler tobacco and filter contained elevated levels of toxic and carcinogenic metals especially, cadmium and lead, and were relatively higher than metal loads in branded cigarettes reported in literature from other developing and developed countries. A comparison of the results obtained through Tessier's fractionation scheme and pseudo-total procedure showed insignificant differences in total metal concentrations of Cd, Cu, Fe, Pb, and Zn. This study provides vital information for international and local health authorities, standard enforcement organizations, and antidrug enforcement agencies, and the general population on the inherent dangers of smoking cigarettes. Relevant agencies must ensure strict regulation of imported and locally produced cigarette and tobacco products. A comprehensive assessment of the contents and the full disclosure of all ingredients in cigarettes and other tobacco products consumed in Nigeria and the potential risks associated with exposure to these ingredients should be communicated to the general population, and especially the cigarette consumers.

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