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Toxic metals distribution in different components of Pakistani and imported cigarettes by electrothermal atomic absorption spectrometer

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ABSTRACT

It was extensively investigated that a significant flux of toxic metals, along with other toxins, reaches the lungs through smoking. In present study toxic metals (TMs) (Al, Cd, Ni and Pb) were determined in different components of Pakistani local branded and imported cigarettes, including filler tobacco (FT), filter (before and after normal smoking by a single volunteer) and ash by electrothermal atomic absorption spectrometer (ETAAS). Microwave-assisted digestion method was employed. The validity and accuracy of methodology were checked by using certified sample of Virginia tobacco leaves (ICHTJ-cta-VTL-2). The percentages (%) of TMs in different components of cigarette were calculated with respect to their total contents in FT of all branded cigarettes before smoking, while smoke concentration has been calculated by subtracting the filter and ash contents from the filler tobacco content of each branded cigarette. The highest percentage (%) of Al was observed in ash of all cigarettes, with range 97.3–99.0%, while in the case of Cd, a reverse behaviour was observed, as a range of 15.0–31.3% of total contents were left in the ash of all branded cigarettes understudy.

1. Introduction

The use of tobacco products constitutes the most significant cause of morbidity and mortality in the world. The smoking of tobacco products has been implicated in the etiology of respiratory diseases, cancer, and cardiovascular diseases related to atherosclerosis [1]. Cigarette smoke contains both organic as well as inorganic human carcinogenic compounds. According to WHO, for every 10 s a person dies as a result of tobacco use [2]. Tobacco-related diseases originate from the biological consequences of repeated inhalation of numerous toxic constituents of cigarette smoke, which are produced by pyrosynthesis or liberated during combustion. Exposure to environmental tobacco smoke (ETS) among nonsmokers increases the risk of subsequent lung cancer, cardiovascular and respiratory problems [3].

Cigarette design has been largely evolved over the last decades with the incorporation of new tobacco processes, papers, filters, and several ingredients (flavor, humectants and casing materials), which either alone or in combination have the potential to modify the quantity and/or the quality of the smoke yielded [4]. The tobacco plant absorbed TMs, most probably from the soil, fertilizing products or from pesticides. Thus, levels of TMs in tobacco are higher when grown in soil containing their high concentrations. Other environmental factors may influence TMs uptake by tobacco plants including soil pH, sewage sludge and fertilizers applied to crops [5]. The most widespread distributed environmental metal poisons include lead, cadmium, mercury, and the metalloid arsenic [6].

Aluminum is present abundantly in tobacco [7]. The most prominent early pathological change associated with Al toxicity is the accumulation of neuro-fibrillar tangles in many regions of the brain. Al also competes with and alters calcium metabolism in several organ systems including the brain [8]. Lead and cadmium are present in tobacco smoke and contribute significantly to cancer risk indices [9]. Cadmium has been found in several studies consistently to transfer into the smoke phase [10–12], which coupled with the fact that the tobacco plant is particularly efficient in accumulating Cd from the soil and translocating most of the metal to the leaves makes this element the prime focus for particular investigation for any potential toxic effects. Lead is a highly toxic metal and is capable of causing serious effects on the brain and bone mineral density [13]. An increase of Pb level is associated with a decrease in the intelligence quotient (IQ) levels and potential behavioural problems. It was reported that Pb in tobacco has been associated

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with impaired fetal growth and brain development [14]. As is the case with cadmium, tobacco plants absorb nickel from the soil and concentrate it in the leaves. In 1990, a working group of the International Agency for Research on Cancer evaluated epidemiologic and experimental studies of nickel-related cancer and concluded that nickel compounds were carcinogenic to humans [15].

The determination of metals in plants has traditionally been performed by digestion with acid or acid mixtures [16], then measuring the elements by a suitable instrumental technique. Sample digestion techniques had a high progress in the last decades mainly due to the development of microwave-assisted digestion systems, which combines high decomposition efficiency and short digestion time [17]. Microwave-assisted digestion offers many advantages than conventional digestion procedures used for food analysis. Microwave digestions are usually performed with nitric acid in a closed high-pressure polytetrafluoroethylene (PTFE) vessel at temperatures above the boiling point of nitric acid. These features lessen acid consumption, contamination, and preparation time [18]. During smoking, the toxic metal content originally present in the filler tobacco (FT) of cigarettes, partitions among the mainstream smoke, sidestream smoke, ash and cigarette or filter. We examined the fraction of Al, Cd, Ni and Pb residing in the ash and filter of cigarette and calculated the smoke phase by difference obtained from total content of analytes in FT of cigarettes of same batch and packet, to avoid the collection of smoke due to tedious methods and material used to collect smoke particulate [19].

The main objective of this work was to evaluate health relevance, to compare the status of toxic metal pollution arising from cigarette smoking and to determine the potential harm they constitute to the environment in Pakistan. Pakistan is an agricultural country. The annual production of tobacco is 70.0–75 million kg, while the domestic requirement is 40–50 million kg, the remaining 30–35 million kg is exported. Tobacco cultivation occupies relatively a small area; about 0.27% of the total irrigated land in Pakistan. Although, cigarettes consumption is falling in most countries of the world but in Pakistan, both production and consumption of this 'silent killer' is increasing at an alarming rate. It must be surprising to note that as the world is fighting against the smoking, but increasing number of Pakistanis are getting hooked, setting new records by manufacturing additional five billion cigarettes each year. The rate of smoking among males is more than 40%, while 7% in females. Presently we evaluated and compared the status of toxic metals (Al, Cd, Ni and Pb), in different pre-smoking and post-smoking components (filler tobacco, filter and ash) of various Pakistani and imported branded cigarettes existing in Pakistan. The results were compared to the literature cited values for other international cigarette brands. Microwave-assisted acid digestion method was applied for the determination of Al, Cd, Ni and Pb, in different components of 12 branded cigarettes. The accuracy of proposed method was evaluated with those obtained with the conventional digestion and also applied on certified reference material.

2. Experimental

2.1. Reagents and glassware

Chemicals used were of analytical grade, ultra-pure water obtained form ELGA labwater system (Bucks, UK) was used throughout the work, 65% nitric acid, 30% hydrogen peroxide and 37% HCl purchased from Merck (Darmstadt, Germany) were used. Certified sample Virginia tobacco leaves (ICHTJ-cta-VTL-2) produced and certified by Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 (Warsaw, Poland) was analysed for validation of digestion methods. Moreover, matrix modifiers were employed to analyse Al (0.2 mg of $Mg(NO_3)_2$), 0.001 mg Pd + 0.0015 mg $Mg(NO_3)_2$ for Cd; 0.2 mg $NH_4H_2PO_4$ for Pb; 0.05 mg $Mg(NO_3)_2$ for Ni, were prepared from $NH_4H_2PO_4$, $Mg(NO_3)_2$ and Pd 99.999% Sigma (St. Louis, MO, USA). Standard solutions of Al, Cd, Ni and Pb were prepared by dilution of certified standard solutions (1000 mg L^{-1}, Fluka Kamica (Bush, Switzerland) of corresponding metal ions. Glasswares and polyethylene containers were soaked in 10% (v/v) HNO_3 for 24 h; washed with distilled water and finally with de-ionized water and dried in such a manner to ensure that no any contamination from glassware occur.

2.2. Instrumentation

Agate ball mixer mill (MM-2000 Haan, Germany), was used for grinding the cigarette tobacco, filter and ash. Sieves made of nylon with mesh sizes of Ø <50 and 65 μm were used to study the influence of particle size on extraction. The analysis of metals was carried out by means of a double beam PerkinElmer atomic absorption spectrometer model 700 (Norwalk, CT, USA) equipped with a graphite furnace HGA-400, pyrocoated graphite tube with integrated platform, an autosampler AS-800 and deuterium lamp as background correction system. Hollow cathode lamps were used as radiation sources. Hollow cathode lamps (PerkinElmer) operating at recommended current were used for all cases. All instrumental conditions were used according o the manufacturer's recommendation. A PEL domestic microwave oven (Osaka, Japan), programmable for time and microwave power from 100 to 900 W, was used for total digestion of samples.

2.3. Sampling

Twelve different commercially available brands, Pakistani (LBCs) and imported cigarettes (IBCs) were purchased from local market of Hyderabad (Pakistan) during 2005, 2006.

The samples were in their original packaging, and placed in pre-washed dried plastic bags separately and stored at −4 °C until tested. The weight of each cigarette after dried at 80 °C was determined. A duplicate four composites samples of each branded cigarette (n = 10) were taken randomly from four different batches (packed on different dates). For analysis of toxic metals in cigarette tobacco, we separated all components of cigarette, tobacco, filter and wrapping paper of five cigarettes of each composite samples and dry it in a sterilized glass beaker for 48 h at 80 °C, the dried tobacco were ground with agate ball mixer mill and sieved through nylon sieves with mesh sizes of Ø 65 μm. The remaining five cigarettes of each corresponding composite batch of all branded cigarettes understudy were used for smoking by a volunteer to collect ash of cigarette in cleaned PTFE beaker separately at room temperature (30–35 °C). Cigarette smoking termination was carrying out when the burning line reached the butt length (different according to different brand). Care was taken to avoid any source of contamination, and this preparation was done in a clean room.

2.4. Microwave-assisted acid digestion

A microwave-assisted digestion procedure was carried out in order to achieve a shorter digestion time. Replicate six samples of each certified and triplicate samples of FT of each cigarette brand (0.2 g), while filter and ash (obtained from each cigarette), were weighed in PTFE flasks (25 mL in volume), added 2.0 mL mixture

Table 1
Validation of the microwave-assisted digestion (MAD) and conventional wet acid digestion (CAD) against certified reference material (Virginia tobacco leaf) ($\mu g\,g^{-1}$, $n = 6$)

Toxic metals	$\bar{x} \pm s$		% R.S.D.	$\bar{x} \pm s$, MAD	% R.S.D.	$t_{critical} = 2.57 t_{Experimental}$
	Certified	CAD				
Al	1680	1680 ± 122	7.26	1640 ± 96.8	5.90	0.288
Cd	1.52 ± 0.171	1.52 ± 0.102	6.71	1.50 ± 0.0781	5.20	0.158
Pb	22.1 ± 0.0772	22.3 ± 0.352	1.57	21.5 ± 0.381	1.77	0.0311
Ni	1.98 ± 0.212	1.97 ± 0.201	10.2	1.95 ± 0.181	9.28	0.275

of concentrated HNO_3–H_2O_2 (2:1, v/v) to tobacco leaves and filter, while acids mixture HNO_3–HCl (1:3, v/v) was used for ash of cigarette, kept all flasks at room temperature for 10 min. Placed flasks in a PTFE container close it and subjected to at 80% of total microwave energy (900 W). After cooling, the contents of each flask were heated on electric hot plate to semi dried mass and dissolved in 5 mL of 1.0 M nitric acid and filtered through Whatman filter paper, the final volume was made up to 10 mL with de-ionized water as stock sample solutions.

2.5. Conventional acid digestion method

For comparison purpose, weighed triplicate 0.2 g of composite cigarette tobacco sample of each batch of different branded homogenized cigarette tobacco while filter and ash of cigarette after smoking of same batch and duplicate samples of certified reference material were placed into PTFE flasks separately. Added 5 mL volume of a freshly prepared mixture of concentrated HNO_3–H_2O_2 (1:1, v/v) to tobacco and filters, while 5.0 mL of HNO_3–HCl (1:3, v/v) were used for ash and allowed to digest on electric hot plate at 80 °C, for 2–3 h, till the clear transparent digests were obtained. After cooling, 5 mL of de-ionized water was added filtered through a Whatman filter paper no. 42 into a 10 mL volumetric flask [20–23]. The final solutions were collected in polyethylene flask, for the determinations of Al, Cd, Ni and Pb by ETAAS.

Blanks measurements were also carried out for both methods. Quantitative analysis was achieved by manipulating the relevant calibration curves prepared from aqueous solutions of metal standards in the same acid concentration to minimize matrix effects. The further dilutions of samples solutions were made according to the concentrations of analytes understudy.

2.6. Statistical analysis of data

All experimental data processing was done with Minitab 13.2 (Minitab Inc., State College, PA) and Microsoft Excel 2000. The results were statistically analysed using Wilcoxon signed rank test; however the significant differences were found among the % smoke, filter and ash of all cigarettes brands.

3. Results and discussion

3.1. Analytical figure of merit

The linear range of the calibration curve reached from the detection limit up to 250, 10, 50 and 100 $\mu g\,L^{-1}$, for Al, Cd, Pb and Ni, respectively. Characteristic masses were 80.0, 1.00, 32.0 and 3.80 pg for Al, Cd, Ni and Pb, respectively. The detection limit (LOD) was defined as $3s/m$, where s is the standard deviation corresponding to 10 blank injections and m is the slope of the calibration graph. The LODs of 1.2, 0.05, 0.15 and 0.55 $\mu g\,L^{-1}$ were calculated for Al, Cd, Ni and Pb, respectively.

Recoveries of target elements were computed by comparison of microwave-assisted method data against values of certified CRM values and the results obtained from a reference analytical method using electric hot plate digestion on same CRM. This method gives comparatively clean extracts than conventional digestion method. Statistical analysis showed that there was no significant difference between the two methods using paired t-test at 95% confidence level with five degrees of freedom (Table 1). The obtained values for all toxic metals in the reference material were in consistence with their certified values and calculated as

$$\%\text{recovery} = \frac{[\,]_{\text{microwave-assisted digestion}}}{[\,]_{\text{certified values}}} \times 100$$

The relative standard deviations for analytes under study in Virginia tobacco leaf were found for CAD and MAD in the range of 1.57–10.2% and 1.77–9.21%.

3.2. Toxic metals in different components of cigarettes

The analysis of different LBCs and IBCs for four TMs in different components of cigarette (filler tobacco, filter) pre-smoking and (filter and ash) post-smoking were determined by ETAAS.

Toxic metals (Al, Cd, Ni and Pb) obtained from filler tobacco, ash and filter of both LBC and IBC origin, showed a wide variation with regard to concentration levels of four TMs. The comparison of results obtained by microwave-assisted digestion with conventional wet acid digestion for analysis of Al, Cd, Ni and Pb in certified reference material showed that differences were not sig-

Table 2
Informations about local and imported branded cigarettes

Sample code	Sample name	Description	Wt/cigarette (g)
LBC1	Diplomat	King size, filter	0.891 ± 0.041
LBC2	Morven Gold	King size, Virginia	0.733 ± 0.032
LBC3	Red & White	King size, filter	0.652 ± 0.024
LBC4	Gold Flake	Wills, King size, filter	0.931 ± 0.011
LBC5	Gold Leaf	King size, Virginia	0.764 ± 0.043
LBC6	Boss	King size, filter	0.624 ± 0.032
LBC7	Channel	King size, Virginia	0.833 ± 0.051
LBC8	Capstan	King size	0.831 ± 0.023
IBC1	Dunhil	International, filter deluxe UK	0.722 ± 0.034
IBC2	Pine	Benhson and hedges	0.575 ± 0.052
IBC3	Marloboro	Filter class A cigarettes (USA)	0.876 ± 0.041
IBC4	More	Menthol filter class A cigarettes (USA)	0.954 ± 0.033

nificant (paired *t*-test) as shown in Table 1. The informations of local branded and imported BCs are given in Table 2. The results of TMs in different component of LBCs and IBCs were expressed as mean ± standard deviation ($\bar{x} \pm s$), as shown in Table 3a–d. The filler tobacco of different LBC and IBC of different batches contains Al, Cd, Ni and Pb concentrations in the ranges of 333–546, 1.66–2.96, 0.725–1.34 and 0.359–1.39 μg/cigarette, respectively. The results indicated that the understudy analytes were not detected in filter before smoking, but were detected in it after smoking. The percentage ranges of Al, Cd, Ni and Pb absorbed and trapped by filter of different branded cigarettes were found at 95% confidence limit [1.38, 2.06%], [8.32, 15.52%], [4.21, 7.35%] and [4.57, 6.61%], respectively, of total metals content observed in FT (Table 3a–d). The percentage of Al, Cd, Ni and Pb in ash of all cigarettes understudy, were observed at 95% CI [97.8, 98.5%], [23.2, 28.7%], [37.2, 40.8%] and [39.7, 42.7%] of total contents in filler tobacco, respectively. The

Table 3
Concentration of aluminum, cadmium, nickel and lead in filler tobacco (FT), filter (F) and ash of different local (LBC) and imported (IBC) branded cigarettes (result based on $\bar{x} \pm s$, μg/cigarette, $n = 10$)

Codes	Filler tobacco	Filter	Ash	Smoke concentration = FT − F + A[a]	Estimated Al/10 cigarette smoke
(a) Aluminum					
LBC1	384 ± 18.5	5.16 ± 0.251 (1.35)[b]	378 ± 25.3 (98.5)[b]	0.505 ± 0.123 (0.132)[b]	5.05
LBC2	373 ± 15.8	6.47 ± 0.313 (1.73)	366 ± 26.5 (98.1)	0.449 ± 0.131 (0.121)	4.50
LBC3	485 ± 29.0	6.67 ± 0.685 (1.37)	478 ± 31.5 (98.5)	0.559 ± 0.153 (0.115)	5.60
LBC4	462 ± 26.6	4.15 ± 0.268 (0.901)	457 ± 32.4 (99.0)	0.480 ± 0.132 (0.104)	4.80
LBC5	333 ± 21.3	8.39 ± 0.568 (2.40)	324 ± 42.5 (97.3)	0.964 ± 0.111 (0.289)	9.64
LBC6	485 ± 38.6	6.64 ± 0.711 (1.37)	478 ± 45.8 (98.5)	0.459 ± 0.124 (0.0954)	4.60
LBC7	546 ± 40.2	10.5 ± 0.991 (1.92)	535 ± 46.3 (98.0)	0.477 ± 0.127 (0.0871)	4.77
LBC8	373 ± 22.1	6.41 ± 0.564 (1.72)	366 ± 32.5 (98.1)	0.569 ± 0.201 (0.153)	5.70
IBC1	486 ± 20.2	7.56 ± 0.452 (1.56)	478 ± 41.5 (98.4)	0.239 ± 0.125 (0.0494)	2.40
IBC2	384 ± 25.4	5.41 ± 0.435 (1.41)	379 ± 12.5 (98.5)	0.289 ± 0.0452 (0.0753)	2.90
IBC3	365 ± 21.7	9.61 ± 0.895 (2.64)	355 ± 35.8 (97.3)	0.342 ± 0.101 (0.0942)	3.42
IBC4	383 ± 30.5	9.38 ± 0.891 (2.45)	373 ± 34.2 (97.4)	0.437 ± 0.0473 (0.114)	4.37

Codes	Filler tobacco	Filter	Ash	Smoke concentration = FT − F + A[a]	Estimated Cd/10 cigarette smoke
(b) Cadmium					
LBC1	2.41 ± 0.161	0.132 ± 0.012 (5.48)[b]	0.620 ± 0.032 (25.7)[b]	1.66 ± 0.145 (68.8)[b]	16.6
LBC2	2.54 ± 0.152	0.213 ± 0.013 (8.40)	0.770 ± 0.051 (30.3)	1.56 ± 0.165 (61.3)	15.6
LBC3	2.49 ± 0.191	0.118 ± 0.013 (4.73)	0.634 ± 0.032 (25.4)	1.74 ± 0.177 (69.8)	17.4
LBC4	2.96 ± 0.114	0.282 ± 0.020 (9.53)	0.930 ± 0.035 (31.3)	1.75 ± 0.123 (59.1)	17.5
LBC5	1.66 ± 0.123	0.255 ± 0.013 (15.3)	0.250 ± 0.032 (15.0)	1.16 ± 0.121 (69.6)	11.6
LBC6	2.80 ± 0.142	0.265 ± 0.012 (9.45)	0.852 ± 0.031 (30.4)	1.69 ± 0.201 (60.1)	16.9
LBC7	2.56 ± 0.171	0.286 ± 0.014 (11.2)	0.684 ± 0.032 (26.7)	1.59 ± 0.117 (62.1)	15.9
LBC8	2.75 ± 0.133	0.225 ± 0.015 (8.18)	0.750 ± 0.023 (27.2)	1.78 ± 0.101 (64.6)	17.8
IBC1	2.07 ± 0.104	0.389 ± 0.014 (18.8)	0.540 ± 0.033 (26.1)	1.14 ± 0.102 (55.2)	11.4
IBC2	1.91 ± 0.110	0.301 ± 0.015 (15.7)	0.550 ± 0.026 (28.7)	1.06 ± 0.115 (55.5)	10.6
IBC3	1.83 ± 0.122	0.373 ± 0.013 (20.3)	0.410 ± 0.016 (22.3)	1.05 ± 0.102 (57.3)	10.5
IBC4	2.01 ± 0.146	0.352 ± 0.012 (17.4)	0.441 ± 0.023 (21.9)	1.22 ± 0.121 (60.8)	12.2

Codes	Filler tobacco	Filter	Ash	Smoke concentration = FT − F + A[a]	Estimated Ni/10 cigarette smoke
(c) Nickel					
LBC1	1.08 ± 0.073	0.0763 ± 0.005 (7.09)[b]	0.391 ± 0.021 (36.3)[b]	0.609 ± 0.052 (56.6)[b]	6.10
LBC2	1.00 ± 0.098	0.0554 ± 0.003 (5.50)	0.356 ± 0.021 (35.3)	0.596 ± 0.045 (59.2)	5.96
LBC3	1.02 ± 0.112	0.0402 ± 0.002 (3.98)	0.410 ± 0.012 (40.3)	0.567 ± 0.043 (55.8)	5.68
LBC4	1.27 ± 0.0911	0.0211 ± 0.002 (1.67)	0.510 ± 0.021 (40.3)	0.735 ± 0.035 (58.0)	7.35
LBC5	1.34 ± 0.081	0.0561 ± 0.003 (4.17)	0.575 ± 0.012 (42.8)	0.713 ± 0.038 (53.1)	7.13
LBC6	1.08 ± 0.071	0.0522 ± 0.008 (4.82)	0.474 ± 0.012 (43.7)	0.558 ± 0.048 (51.5)	5.59
LBC7	1.06 ± 0.091	0.0473 ± 0.005 (4.43)	0.410 ± 0.013 (38.6)	0.605 ± 0.049 (57.0)	6.05
LBC8	1.04 ± 0.082	0.0394 ± 0.005 (3.79)	0.413 ± 0.012 (39.8)	0.585 ± 0.043 (56.4)	5.85
IBC1	0.980 ± 0.086	0.0721 ± 0.004 (7.37)	0.400 ± 0.022 (40.8)	0.507 ± 0.036 (51.8)	5.08
IBC2	0.725 ± 0.065	0.0730 ± 0.002 (10.1)	0.250 ± 0.011 (34.5)	0.402 ± 0.042 (55.4)	4.02
IBC3	1.12 ± 0.095	0.0982 ± 0.001 (8.77)	0.391 ± 0.021 (34.9)	0.632 ± 0.034 (56.4)	6.33
IBC4	0.962 ± 0.087	0.0731 ± 0.0027 (7.61)	0.383 ± 0.011 (39.8)	0.506 ± 0.047 (52.6)	5.06

Codes	Filler tobacco	Filter	Ash	Smoke concentration = FT − F + A[a]	Estimated Pb/10 cigarette smoke
(d) Lead					
LBC1	1.39 ± 0.075	0.0683 ± 0.002 (4.91)[b]	0.580 ± 0.035 (41.6)[b]	0.745 ± 0.056 (53.5)[b]	7.45
LBC2	0.894 ± 0.051	0.0274 ± 0.005 (3.07)	0.385 ± 0.0236 (43.1)	0.481 ± 0.051 (53.8)	4.81
LBC3	0.959 ± 0.061	0.0473 ± 0.002 (4.93)	0.420 ± 0.0131 (43.8)	0.492 ± 0.056 (51.3)	4.92
LBC4	1.27 ± 0.071	0.0671 ± 0.005 (5.27)	0.540 ± 0.023 (42.4)	0.665 ± 0.066 (52.3)	6.65
LBC5	0.889 ± 0.054	0.0425 ± 0.003 (4.78)	0.362 ± 0.011 (40.7)	0.485 ± 0.023 (54.5)	4.85
LBC6	0.915 ± 0.072	0.0494 ± 0.006 (5.40)	0.350 ± 0.021 (38.2)	0.516 ± 0.045 (56.4)	5.16
LBC7	0.926 ± 0.076	0.0528 ± 0.005 (5.70)	0.360 ± 0.015 (38.9)	0.513 ± 0.032 (55.4)	5.13
LBC8	1.06 ± 0.092	0.0363 ± 0.007 (3.43)	0.485 ± 0.033 (45.7)	0.539 ± 0.042 (50.8)	5.39
IBC1	0.881 ± 0.051	0.0641 ± 0.008 (7.26)	0.350 ± 0.015 (39.7)	0.467 ± 0.025 (53.0)	4.67
IBC2	0.399 ± 0.021	0.0310 ± 0.004 (7.78)	0.131 ± 0.010 (32.9)	0.237 ± 0.012 (59.3)	2.37
IBC3	0.611 ± 0.031	0.0420 ± 0.009 (6.88)	0.245 ± 0.013 (40.1)	0.289 ± 0.021 (53.0)	2.89
IBC4	0.821 ± 0.071	0.0520 ± 0.011 (6.34)	0.320 ± 0.010 (39.0)	0.449 ± 0.031 (54.7)	4.49

[a] Concentration of TMs in smoke obtained from total content in filler tobacco minus concentration of filter and ash values of same cigarette.
[b] Values in parenthesis is (%) of toxic metals in different component of cigarette with related to total contents in filler tobacco.

concentration of toxic metals in FT were higher than those in the ash, these results are consistent with other study [24]. Cigarette ash plays an important role in terms of toxic metal distribution towards human health and environmental pollution. Al was found to have divergent concentration values in the different components of LBC, maximum concentration was found to be 546 μg/cigarette in Channel where as a minimum concentration of Al (333 μg/cigarette) was obtained for Gold Leaf, although major amount of Al was left in ash ranged as 324–534 μg/cigarette (Table 3a). In case of IBC the lowest Al concentration 365 μg/cigarette, was found in Marlboro. It was observed that the concentration of Al is not different significantly ($p > 0.05$) according to LBC and IBC. It was also observed that Al concentration is very low in smoke, corresponding to only 0.049–0.289% as compared to total content in filler tobacco of different cigarettes. The changes in the composition of tobacco, ash and filter from cigarettes of various brands are associated with peculiarity of tobacco plant varieties and tobacco processing. There is no significant different in average concentration of Cd in all branded cigarettes tested (ranging from 1.66 to 2.96 μg/cigarette; Table 3b). The minimum amount of Cd was observed in LBC (Gold Leaf), while highest amount was also observed in LBC (Gold Flake and Boss). As compared with the reported results for Cd in the United Kingdom (0.90 $\mu g\,g^{-1}$) and Korean cigarettes (1.02 $\mu g\,g^{-1}$), the average Cd contents in LBC are 2.53 and 2.26 times higher than those of United Kingdom and Korea, respectively [25], but lower than some branded cigarettes of Jordan [26]. Lead concentration in filler tobacco of LBC was higher as compared to concentration of Pb observed in foreign brands IBC, while these values are consistence with Pb concentration in cigarettes of other developed countries.

Toxic metal uptake by tobacco plants depends on the concentration of these toxicants in the soil, soil amendments with sewage sludge and soil pH [27]. The uptake of TMs by varieties of agricultural products has been shown to be dependent on geographical origin [28]. The investigated data indicates that smokers could receive significantly higher exposures to various toxic and carcinogenic metals from different LBC and IBC. Since Al has been found in all of the major cigarette components, one would imagine that smoking could be one source of Al exposure. Aluminum has a fixed oxidation number, and therefore cannot participate in redox reactions. However, as cited above, Al can displace iron from binding sites, and hence, results in an increase in catalytically active iron [29]. Thus, Al in tobacco smoke may enhance iron-dependent free radical-induced tissue damage via an indirect mechanism [30]. Tobacco plants have a profound ability to absorb cadmium from the soil and accumulate it in high concentrations in the leaves and can lead to human exposure to this carcinogenic metal [31]. Cadmium is the best studied metal from cigarette smoke, and smoking is the main source of Cd intake by humans. The content of Cd in cigarettes and cigarette smoke was analysed in a number of studies. Although the Cd amounts varied, the average Cd content per cigarette lies between 0.5 and 1.5 mg/cigarette [32].

Lead may also be present in high concentrations in tobacco smoke. Smokers have considerably higher blood lead levels than nonsmokers [33]. Nickel reacts with carbon monoxide in tobacco smoke to form a highly toxic carbonyl compound, which is believed to be a potential carcinogen. The amount of Ni in the tobacco plant lies between 0.640 and 1.15 $mg\,g^{-1}$, and varies greatly in cigarettes of different brands [34].

There was good agreement for levels of Al, Cd, Pb and Ni in each Pakistani (LBC) and imported branded cigarettes (IBC), purchased from local vendors of Pakistan. The amount of these toxic metals passed to the smokes of 10 cigarettes of different brands were estimated to be 2.40–9.64, 10.5–17.8, 4.02–7.35 and 2.37–7.45 μg/10 cigarettes, respectively, either passed into mainstream or sidestream smoke. These variations could possibly be attributed to soil contents of these TMs on which tobacco was cultivated, type of tobacco, growth conditions and tobacco treatment process. The potential health impact from smoking cigarettes that deliver high levels of TMs is not limited to active smokers. It was investigated that one pack of cigarettes deposits 2–4 μg Cd into the lungs of a smoker whereas some of the smoke passes into the air to be inhaled by smokers and nonsmokers alike [35]. Our results showed that by smoking 10 cigarettes a day, approximately, 9.64, 17.8, 7.35 and 7.45 μg of Al, Cd, Ni and Pb, respectively/person/day is inhaled by the smoker or spreads into the environment.

4. Conclusion

In present study, the microwave acid digestion method followed by ETAAS had been successfully applied for the determination of Al, Cd, Ni and Pb from different components of cigarettes. There is no sufficient data about the toxic metals concentrations in different LBC and IBC in Pakistan. This study provided a new data for the health authorities in Pakistan such as the Ministry of Health and Ministry of Environment. The results of TMs in different branded cigarettes consumed in Pakistan, confirmed that tobacco is a notable source of TMs pollutants and most importantly the major source of TMs exposure to the general population. Except a few LBC, there is no significant difference in concentration of these toxic metals in both local and imported cigarettes. Elevated levels of Al, Cd, Ni and Pb in cigarettes tobacco do not necessarily indicate that such products bestow additional risk to those already associated with tobacco use. However, elevated levels of toxic metals in tobacco products demand further evaluation from a public health standpoint.

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