Original Article

Mercury, cadmium, and lead in cigarettes from international markets: concentrations, distributions and absorption ability of filters

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ABSTRACT — Mercury (Hg), cadmium (Cd), and lead (Pb) concentrations in marketed cigarettes from South Korea, Vietnam, Japan, Indonesia, Taiwan, Thailand, the United Kingdom (UK), Belgium, Italy, Finland, and France were investigated. The cigarettes from Vietnam and Thailand had the highest trend of Hg. Meanwhile, Cd was found higher in cigarettes from Thailand, the UK, and Belgium. Pb concentrations in cigarettes from Belgium, the UK, and Korea were higher than others. The average of these heavy metals concentrated in cigarettes was in the order of Pb > Cd > Hg. Furthermore, the contents of these heavy metals in cigarette leaves were much higher than in filter and rolling paper. There was a significant positive correlation between Hg and Cd, but no correlation between Cd and Pb and between Hg and Pb. Significant positive correlations of nicotine with Hg and Cd but not Pb in the cigarette were observed. Activated carbon filters (Ce-C) absorb Cd and Pb from cigarette leaves and rolling paper indicated a higher trapping trend than cellulose acetate filter without activated carbon (Ce). The trapping ratios of Ce-C (Cd: 5.53%, Pb:5.41%) were higher than Ce (Cd:3.09%, Pb:5.49%). On the other hand, Hg had lower absorption by both types of filters (Ce:0.15%, Ce-C:0.02%). This revealed that Hg, Cd and Pb absorption ability by both filters was relatively lower to the total concentration of these metals in tobacco leaves and rolling paper. The concern was that the higher concentrations of metals such as Hg, Cd and Pb in cigarettes might exist in mainstream smoke.

Key words: Cigarettes, Distribution, Heavy metals, Mercury, Cadmium, Lead

INTRODUCTION

Tobacco has been used in the world for thousands of years by humans. Tobacco and its smoke contain more than 4000 different substances, including various carcinogens and toxic metals (Stratton *et al.*, 2001). As a crop, tobacco is considered an indicator of environmental pollution. Air pollutants damage food crops' yield and nutritional quality and safety, imposing a major risk to food safety. In addition to this, the soil parent material is the

most important influencing factor of heavy metal concentrations, and human activities are the main external sources of heavy metals (Wu *et al.*, 2020). Around 6.5 trillion cigarettes are sold worldwide each year, which translates to roughly 18 billion cigarettes per day (Martin, 2019). Furthermore, tobacco kills more than 8 million people each year. More than 7 million deaths result from direct tobacco use, while around 1.2 million result from non-smokers being exposed to secondhand smoke (World Health Organization, 2019). In particu-

lar, tobacco is strongly identified as a source of cadmium (Cd) exposure in humans. Humans are also exposed to lead (Pb) vapors through inhalation. Pb from cigarette smoke (including second and third-hand tobacco smoke exposures) may increase blood Pb levels in children (Agency for Toxic Substances and Disease Registry, 2019). The research data on mercury (Hg) in the cigarette is still limited; meanwhile, the effect of Hg on human health has been known to mainly affect the nervous system, seriously affecting the fetus if exposed to mercury from the mother. Therefore, a study investigating Hg, Cd, and Pb concentrations in commercial cigarettes from many regions and countries is needed. These data will contribute to the management and prevention of tobacco-related harms to the community and human health.

Recently, several studies on heavy metals in tobacco have been implemented. Ziarati *et al.* (2017) indicated that Cd and Pb are found in cigarette tobacco, showing that the tobacco plant easily takes up metals from soil and concentrates them in leaves. This report published that the ratios of Cd and Pb absorbed and trapped by filters were 116-234% and 112-198%. From these results, the cigarette filters had very high absorbing abilities of Cd and Pb by cigarette filter, even higher than 100%. In other research, an extensive investigation of 42 elements, including trace elements in the blood of non-smokers, cigarette smokers, and e-cigarettes users, was implemented and this showed that the content of elements in cigarette smokers had the highest concentrations of copper (Cu), molybdenum (Mo), zinc (Zn), antimony (Ab), and strontium. The e-cigarette users presented the highest levels of selenium (Se), silver (Ag), and vanadium (V) (Badea *et al.*, 2018). These studies showed that cigarette smoke might be an important source of metal exposure in humans. Yurdakök, (2015) recommended that research on Pb, Hg, and Cd in breast milk should aim to reduce life-long exposure through precautionary measures such as prevention of exposure to cigarette smoke, use of unleaded gasoline, and prevention of air pollution with an effect at the community level. Artisanal and small-scale gold mining is known to be the major anthropogenic source of Hg pollution globally due to the direct use of Hg in the gold mining processes (Norvisa *et al.*, 2019; Addai-Arhin *et al.*, 2021). Besides, the improper management of factories or equipment containing mercury also leads to Hg leakage into the environment that is toxic to humans and the ecosystem (Bai *et al.*, 2017; United Nations Environment, 2019). Hg is volatile even at room temperature, making it a global pollutant. Kowalski and Wiercinski (2009) reported that Hg was found in tobacco cigarettes and

ranged from 2.95-10.2 ng Hg per single cigarette. Almost all mercury contained was released into the smoke (from 86.7 to 100%). However, they used a "mechanical lip" model to determine the mercury concentration in cigarette smoke. Airflow interruption by balancing the pump valve connected to the pump syringe leads Hg separately to mainstream and side-stream smoke. Therefore, the absorption of mercury by the filter had not been fully evaluated. Heavy metal analysis in cigarette smoke is still hampered by the loss of smoke flow and smoking process descriptors' entanglement. Tobacco smoke analysis is also susceptible to cross-contamination of samples when conducting experiments. Therefore, this affects test results and is difficult to perform on many samples.

Thus, the aims of this study were to first (1) investigate concentrations of heavy metals, including Hg, Cd, and Pb, in marketed cigarettes collected from retail sale stores in several countries, including South Korea (Korea), Japan, Taiwan, Thailand, Vietnam, Belgium, France, Italy, Finland, and the United Kingdom (UK), and second, (2) analyze the distribution concentrations of Hg, Cd, and Pb in parts of the cigarette (cigarette filter, tobacco, and rolling paper). The correlations of nicotine concentration with Hg, Cd, and Pb in tobacco also were discussed. Furthermore, the absorption ability of Hg, Cd, and Pb from tobacco after smoking by filter materials was observed. Through that, we assessed the transfer of these heavy metals from cigarette to smoke.

MATERIALS AND METHODS

Sampling and pretreatment

Sixty-seven samples of marketed cigarettes were collected from convenience stores in several countries in the world through 2019. In Asia, 52 cigarette samples were collected (Korea: $n=10$, Vietnam: $n=9$, Japan: $n=10$, Indonesia: $n=13$, Thailand: $n=4$, and Taiwan: $n=6$) while 15 samples were collected from Europe (Belgium: $n=3$, France: $n=3$, Italy: $n=3$, Finland: $n=3$, and the UK: $n=3$). In each country, the samples were collected from different brands of cigarettes. There were several cigarette brands of the same brand but that were collected from different countries. However, information from the cigarette labels indicated that the manufacturers were in the cigarette home country. The label claims of nicotine concentration in the cigarette were recorded. Cigarette samples were dried at room temperature for two days, then homogenized using mortar and pestle. The homogenized cigarette samples were packaged in polypropylene tubes and kept at 4°C in a refrigerator until analysis.

To comprehend Hg, Cd, and Pb's fate in parts of a cig-

Fig. 1. Model of smoking. A - cigarette, B - sample boat for ash accumulation, C - water scrubber, D - pump.

arettte after smoking, we conducted an analysis of these heavy metals in filters and the ash after smoking, using a physical model of smoking (Fig. 1). In this case, a rubber tube was connected to the filter of the cigarette. The pump was run non-stop, the tobacco was burned until finished to keep all the smoke through the filter. Therefore, this experiment conducted a survey only in the mainstream smoke to estimate tobacco's transfer abilities to smoke.

Mercury, cadmium, and lead analysis methods

Mercury analysis method

Approximately 50 mg sample was weighed using an analytical/electronic balance (Practum124-1SJP, Satorius, Göttingen, Germany). Hg was determined using pyrolysis atomic absorption spectrometry with gold amalgamation by a model of mercury analyzer 3000 (Nippon Instrument Corporation, Tokyo, Japan). Hg was determined at a wavelength of 253.7 nm by thermal combustion. The oxygen gas was purchased from Kumamoto Sanso Corporation (Kumamoto, Japan), and the flowing gas was set at 0.2 L/min. Two calibration curves were prepared using a Hg standard solution (1000 mg/L, Wako Pure Chemical Company, Osaka, Japan), to calculate Hg concentration in samples. The low calibration curves were prepared at six points of 0.2, 0.5, 1, 5, 10, and 20 ng Hg, and the high calibration curves were prepared at six points of 10, 20, 50, 100, 200, and 500 ng of Hg. The calibration curves were described based on the real Hg concentration of analysis with the area of absorbance (ABS) from the atomic absorption spectroscopy of a mercury analyzer (MA 3000, NIC, Tokyo, Japan). The correlation coefficients were 0.9999 for both calibration curves at high and low Hg concentrations. The method

limit of detection (MDL) was calculated using the formula: 3SD of a blank sample ($n = 20$), while the method limit of quantification (MQL) was calculated using 10SD. The MDL and MQL values for the Hg analysis method in cigarette leaf were informed at 0.03 ng/g and 0.09 ng/g, respectively.

Cadmium and lead analysis method

Cadmium and lead concentrations were determined using the method described by Shaheen *et al.* (2016). Approximately 0.5 g of cigarette samples were weighed into Teflon vessels, and 6 mL of 69% nitric acid (HNO_3) and 2 mL of 30% hydrogen peroxide (H_2O_2) (Wako Pure Chemical Company) were added. The mixture was digested using a microwave digestion system (Milestone MLS 1200 Mega, Sorisole, Italy). The digested solution was transferred into the volumetric flask and increased to 50 mL by adding ultrapure water (Barnstead Smart2Pure, ThermoFisher Scientific, Waltham, MA, USA). The solution was filtered using a membrane filter (DISMIC®-25HP PTFE, 0.45 μm , Toyo Roshi, Tokyo, Japan) and stored in 50 mL polypropylene tubes at 4°C until analysis.

Cd and Pb in the digested solution were determined using graphite furnace atomic absorption spectroscopy GF-AAS Z-2700 (Hitachi High-Technologies Corporation, Tokyo, Japan) at wavelengths of 228.8 nm and 283.3 nm, respectively. Approximately 10 μL digested solution was automatically injected into the pyro tube HR (Hitachi High-Technologies Corporation). Then, 10 μL of Palladium Magnesium solution used as Matrix Modifier (Hitachi High-Technologies Corporation) was added to the pyro tube. The pyro graphite tube temperature for Cd and Pb atomization was set at 1500°C and 2000°C, respectively. The argon gas was purchased from Kumamoto Sanso Corporation, and the flow gas was set at 200 mL/min. The calibration curves for Cd and Pb were obtained at standard concentrations of 0; 0.2; 0.5; 1; 2; and 5 $\mu\text{g/L}$ and 0; 1; 2; 5; 10; and 20 $\mu\text{g/L}$, respectively, using multielement standard solution 6 for ICP (Sigma-Aldrich, Postfach 9471, Buchs SG, Switzerland). The correlation coefficients (R^2) of Cd and Pb's calibration curves were 0.9991 and 0.9994, respectively. The MDL and MQL for the method of analysis Cd in cigarette leaf were informed at 0.02 ng/g and 0.06 ng/g, respectively. Furthermore, the MDL and MQL for the analysis method of Pb were 0.09 ng/g and 0.28 ng/g, respectively.

Quality assurance and control

Reagents and experiment tools were under tight control and avoided cross-contamination. All reagents used

were of analytical grade and of highest purity. All experiment tools needed to be cleaned before use. In detail, in the Cd and Pb analysis, before use the experiment tools were washed with tap water, kept in HNO_3 5% overnight, and washed one more time by ultrapure water. Then, the tools were dried for 4 hr using a drier oven. For Hg, after cleaning by soap and ultrapure water, sample boats were kept in a furnace for 5 hr at 750°C to remove remaining Hg. The pyro graphite tube used to analyze Cd and Pb was cleaned at 1800°C and 2200°C after sample atomization in the furnace graphite AAS system after each analysis. The accuracy and precision of analyses were validated by measuring the Hg, Cd, and Pb in triplicate of the subsample, blank samples, and before and after each group of nine samples measurement. The Hg, Cd, and Pb spiked samples were analyzed together with real samples, the recoveries of Hg, Cd, and Pb were confirmed to range from 91% to 105%.

Statistical analysis

Statistical analysis was carried out using IBM® SPSS® Statistics Version 26 (IBM Corporation, New York, NY, USA). In these, all correlation comparisons used Spearman's correlation test (two-tailed). The differences in the mean content of the same metal in the same filter materials of the cigarettes before and after smoking were compared using paired sample t-test (two-tailed). The differences in the mean content of the same metal in different filter materials of cigarettes before and after smoking were also compared using an independent samples t-test (two-tailed).

RESULTS AND DISCUSSION

Cigarette properties

The filtered cigarette is made from three main parts: cigarette filter, roll paper, and tobacco. According to our investigation, in the markets, some brands did not have a filter. However, all collected samples contained a filter. There was an average 0.829 ± 0.129 g/cigarette (tobacco leaf: 0.633 ± 0.098 g/cigarette; filter: 0.158 ± 0.050 g/cigarette; and roll paper: 0.038 ± 0.006 g/cigarette). Tobacco accounted for 76.36% of the total weight of the whole cigarette on average. Filters and rolling paper accounted for 19.06% and 4.58% of one filtered cigarette's total weight, respectively. The nicotine concentration in cigarettes was taken from the package label of the cigarette. The cigarettes that were collected from Korea, Japan, Taiwan, and Indonesia had nicotine concentration indicated on the package label. In contrast, those bought from Vietnam, Thailand, the UK, Belgium, Fin-

land, and France did not indicate nicotine concentration. According to the label's information, the average nicotine concentration in cigarettes collected from these countries was 0.78 ± 0.6 mg/cigarette (0.1-2.3 mg/cigarette). The average nicotine concentrations in the cigarettes were in the order: Korea (nicotine: 0.31 ± 0.18 mg/cigarette) < Japan (0.54 ± 0.25 mg/cigarette) < Taiwan (0.56 ± 0.21 mg/cigarette) < Indonesia (1.54 ± 0.49 mg/cigarette). These results showed that the smoker habit of the cigarette with nicotine concentrations was different in each country. The cigarettes collected from Indonesia had a higher dose of nicotine than other countries, indicating a preference for smoking with high nicotine doses in Indonesian smokers. Korean cigarettes had relatively low nicotine levels in the region, whereas Japan and Taiwan have slightly higher levels of this ingredient in cigarettes. Nicotine is highly addictive and is made by several types of plants such as *Nicotiana tabacum* and is also produced synthetically (Holbrook, 2016; Siqueira *et al.*, 2017). It can cause an increase in blood pressure, heart rate, blood flow to the heart, and a narrowing of the arteries (vessels that carry blood). Smokers who tend to use nicotine levels to increase pleasure after smoking means an increase in tar levels in cigarettes. This puts them at increased risk of adverse health effects due to nicotine, particularly in cigarettes and tobacco in general.

The distribution of mercury, cadmium, and lead in cigarette

Based on the experiment layout, after smoking, the cigarette left ash, smoke, and filter. Thus, we supposed that Hg, Cd, and Pb from tobacco leaves and rolling paper go to three pathways: to be trapped by filter, to remain in the ash, and to transfer to smoke. Therefore, we estimated the ratio of Hg, Cd, and Pb from one cigarette to smoke after smoking.

The distribution of Hg, Cd, and Pb concentrations in parts of cigarettes is shown in Table 1. The mean concentrations of Hg, Cd, and Pb in tobacco of cigarette samples were 19.95 ± 4.8 ng/g, 1.34 ± 0.59 $\mu\text{g/g}$, and 2.30 ± 2.64 $\mu\text{g/g}$, respectively. The filter contained mean concentrations of 0.13 ± 0.13 ng/g, 0.04 ± 0.05 $\mu\text{g/g}$, and 0.05 ± 0.07 $\mu\text{g/g}$ of Hg, Cd, and Pb, respectively. For rolling paper, Hg was not detected (< MDL), while mean concentrations of Cd and Pb were 0.08 ± 0.11 $\mu\text{g/g}$ and 0.26 ± 0.24 $\mu\text{g/g}$, respectively. The results showed that Hg, Cd, and Pb in cigarettes are mostly contained in tobacco leaf. As discussed above, tobacco accounted for an average of 76.36% of the total weight of the whole cigarette, indicating that these heavy metals in cigarettes mainly come from tobacco. In addition, tobac-

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Table 1. Comparison of Hg, Cd, and Pb in parts of cigarette.

Part of cigarette	Before smoking (Mean $\pm$ SD)			After smoking (Mean $\pm$ SD)		
	Hg (ng/g)	Cd (μ g/g)	Pb (μ g/g)	Hg (ng/g)	Cd (μ g/g)	Pb (μ g/g)
Tobacco leaves	19.95 $\pm$ 4.8	1.34 $\pm$ 0.59	2.30 $\pm$ 2.64	NA	NA	NA
Paper	< MDL	0.08 $\pm$ 0.11	0.25 $\pm$ 0.24	NA	NA	NA
Ash	NA	NA	NA	< MDL	0.62 $\pm$ 0.42	< MDL
Filter	0.13 $\pm$ 0.13	0.04 $\pm$ 0.04	0.04 $\pm$ 0.07	0.26 $\pm$ 0.24	0.35 $\pm$ 0.25	0.97 $\pm$ 0.92

< MDL: below method detection limit, NA: not available.

co is made from the leaf of the tobacco plant (*Nicotiana tabacum*). These heavy metals are absorbed from the soil by the plant's roots and transported to the leaf. However, the percentage concentrations of Hg, Cd, and Pb in cigarette paper and filters are relatively lower. Toxic heavy metals are the major source of environmental pollution in this new millennium. Hg, Cd, and Pb are the most common toxic heavy metals in the environment (Yurdakök, 2015). This explains the presence of these heavy metals in cigarette rolling papers and filters at low concentrations.

As discussed above, Hg, Cd, and Pb are mostly contained in tobacco at different concentrations. The concentrations of Hg, Cd, and Pb in tobacco are shown in Fig. 2. The result showed that these heavy metals in tobacco occur in the order of Pb > Cd > Hg. In all sam-

ples, the concentration of Hg was much lower than Cd and Pb. The cigarette samples collected from Korea, Vietnam, Indonesia, the UK, and Belgium contained a higher amount of Pb than Cd. However, Cd concentration was higher than Pb in cigarette samples collected from Japan, Taiwan, Thailand, Italy, Finland, and France. The results showed that Hg, Cd, and Pb concentrations in tobacco cigarettes from these countries are non-uniformly distributed. For Cd, the highest concentrations in tobacco of cigarettes were found in cigarettes from Thailand ($2.48 \pm 0.96 \mu\text{g/g}$), the UK ($1.96 \pm 0.82 \mu\text{g/g}$), and Belgium ($1.8 \pm 0.69 \mu\text{g/g}$). The lowest Cd concentrations were found in cigarettes from Italy ($0.65 \pm 0.15 \mu\text{g/g}$), Japan ($0.67 \pm 0.13 \mu\text{g/g}$), and Indonesia ($0.70 \pm 0.13 \mu\text{g/g}$). In contrast, the highest concentrations of Pb in tobacco were in cigarettes from

Fig. 2. The concentration of Hg, Cd, and Pb in tobacco of cigarettes. The Cd and Pb data are shown in the concentration of $\mu\text{g/g}$ (left vertical axis); the concentration of Hg is shown in ng/g (right vertical axis). Data are represented as Mean $\pm$ SD.

Belgium ($8.34 \pm 0.44 \mu\text{g/g}$), the UK ($5.6 \pm 0.86 \mu\text{g/g}$), and Korea ($4.41 \pm 2.46 \mu\text{g/g}$). Notably, one cigarette sample from Indonesia had the highest Pb concentration of $14.5 \mu\text{g/g}$. However, the average Pb concentration of all cigarettes from Indonesia was $1.58 \pm 3.90 \mu\text{g/g}$. The cigarettes that were sampled from Japan ($0.43 \pm 0.17 \mu\text{g/g}$), Taiwan ($0.61 \pm 0.14 \mu\text{g/g}$), Italy ($0.48 \pm 0.1 \mu\text{g/g}$), Finland ($0.6 \pm 0.03 \mu\text{g/g}$), France ($0.69 \pm 0.23 \mu\text{g/g}$) had a low concentration of Pb. In the case of Hg, the results showed that Hg concentration in tobacco was much lower than Cd and Pb. The Hg in tobacco was found at ppb concentration (ng/g), while Cd and Pb were found at ppm concentration ($\mu\text{g/g}$). The highest total Hg concentration in tobacco was found in cigarettes from Thailand (average: $27.80 \pm 1.06 \text{ ng/g}$), Vietnam (average: $27.23 \pm 6.69 \text{ ng/g}$), Belgium (average: $23.56 \pm 6.88 \text{ ng/g}$). Hg concentrations in tobacco of cigarettes from these countries were higher than those of Korea (average: $20.89 \pm 3.48 \text{ ng/g}$), Finland ($19.66 \pm 1.58 \text{ ng/g}$), Japan (average: $18.38 \pm 2.6 \text{ ng/g}$), France (average: $18.01 \pm 1.68 \text{ ng/g}$), and the UK (average: $17.72 \pm 1.92 \text{ ng/g}$) who also had similar Hg concentrations in tobacco of cigarettes. Meanwhile, the Hg in tobacco of cigarettes from Indonesia (average: $14.19 \pm 2.77 \text{ ng/g}$) and Italy ($12.37 \pm 0.81 \text{ ng/g}$) recorded the lowest concentrations. In this study, the source of tobacco raw material was not investigated. However, it is supposed that the tobacco material from different countries has different Hg, Cd, and Pb pollution levels in the environment, such as in the soil, in drainage water, in fer-

tilizer used for tobacco cultivation. Regardless of the different concentrations of these metals, their cigarette content is remarkable because these heavy metals in the cigarettes have negative health effects on both primary and secondary smokers following continuous exposure.

Based on Hg, Cd, and Pb's concentration in parts of cigarettes, the amount of Hg, Cd, and Pb per one cigarette was also evaluated (Fig. 3). The results showed that the average content of Hg, Cd, and Pb per one cigarette was $12.34 \pm 2.77 \text{ ng/cigarette}$, $0.94 \pm 0.38 \mu\text{g/cigarette}$, and $1.62 \pm 0.74 \mu\text{g/cigarette}$, respectively. It was realized that the higher the concentration of Hg, Cd, and Pb in tobacco of cigarettes and the higher the weight of the cigarette, the greater the concentration of the heavy metals per one cigarette. All the cigarettes contained an amount of tobacco below one gram, the reason that Hg, Cd, and Pb levels in a cigarette are lower than their respective evaluated concentrations ($\mu\text{g/g}$; ng/g). The weight of the cigarette was indicated by the manufacturer on the package label. Generally, the cigarettes from Indonesia had the highest weight of tobacco ($897.40 \text{ mg/cigarette}$). Also, the Hg, Cd, and Pb concentrations in tobacco and per one cigarette were the same trends that reflected the distribution of these heavy metals mostly in tobacco of cigarettes.

The correlations between Hg, Cd, and Pb are shown in Fig. 4. The results showed a significant correlation between Hg and Cd ($r = 0.541$, $p < 0.001$). Meanwhile, the correlations between Hg and Pb and between Cd and Pb were not significant ($r = 0.059$ and 0.095 , respective-

Fig. 3. The concentration of Hg, Cd, and Pb in a cigarette. The Cd and Pb data are shown in the concentration of $\mu\text{g/cigarette}$ (left vertical axis); the concentration of Hg is shown in ng/cigarette (right vertical axis). Data are represented as Mean $\pm$ SD.

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Fig. 4. The correlation of Cd, Cd, and Pb concentration in the cigarette. (a: correlation between Hg and Cd, b: correlation between Hg and Pb, c: correlation between Cd and Pb).

ly, $p > 0.01$). Although there was no clear correlation between heavy metals in the plant in general, the authors supposed the concentrations of Hg, Cd, and Pb in environmental factors such as soil, water, fertilizer can be absorbed by tobacco plants at the same rate if these heavy metals come from the same pollution sources. The correlation between Hg with Cd is significant and may have a similar absorption mechanism within the tobacco plant.

Comparison of Hg, Cd, and Pb concentration in the cigarettes of the present study with other studies is shown in Table 2. The Hg in marketed cigarettes from some previous studies in the United States of America (Panta *et al.*, 2008; Swani *et al.*, 2009; Fresquez *et al.*, 2015), Canada (Hammond and O'Connor, 2008), and Poland (Kowalski and Wiercinski, 2009) showed that the Hg concentrations in cigarettes from these studies are almost equal to those of the present study. Hg in cigarettes was primarily found at ppb (µg/g) concentration. Hg, Cd, and Pb concentrations in cigarettes from the selected countries in this study are almost equal to other studies. However, the Cd and Pb in cigarettes from Nigeria ranged from 5.90-7.94 µg/g and 17.21-74.78 µg/g (Benson *et al.*, 2017), and are much higher than this study. Due to Cd and Pb's high concentration, the Nigeria study showed that cancer health risk through inhalation was significant. In addition, cigarettes from Pakistan contained Pb at an average of 14.39 µg/g (Ajab *et al.*, 2008), which is higher than the present study. Cd in cigarettes from Ethiopia (mean: 6.07 µg/g) is also much higher than that of the present study (Engida and Chandravanshi, 2017).

The correlations of nicotine with Hg, Cd, and Pb concentration in cigarettes

There were significant positive correlations of nicotine with Hg and Cd concentrations in tobacco of cigarettes but not Pb (Fig. 5). The r values of correlations of nicotine with Hg and Cd were 0.564 and 0.451, respectively, and significant ($p < 0.01$), while the r -value correlation of nicotine with Pb was 0.008. The results showed that the correlations between nicotine and these heavy metals are similar. The significant correlations of nicotine with Hg and Cd cause tobacco absorption from environmental factors. The mechanism within the tobacco plant for absorption of Hg and Cd from the environment such as soil, water, and fertilizer may be similar to that of nicotine. Other studies reported that the nicotine concentration in tobacco is closely correlated with the amount of nitrogen supplied (Wang *et al.*, 2008). Nitrogen is present naturally in soils as nitrate ions, ammonium ions, and as a component of soil organic matter. Ammonium is readily converted to nitrate in all but the wettest and driest soils. Nitrogen generally produces the greatest growth response in plants of all fertilizer nutrients (Davies *et al.*, 2001). On the other hand, the fertilizer may contain heavy metals like As, Cd, Cr, Ni, and Hg, which can be transferred to tobacco and be correlated with nicotine concentration (O'Connor *et al.*, 2015). Therefore, some percentage of Hg and Cd content in tobacco may have resulted from fertilizer application to the soil upon which the tobacco

Table 2. Hg, Cd, and Pb content in tobacco of marketed cigarettes from the selected countries.

Country	Heavy metal concentration			References
	Hg (ng/g) Mean $\pm$ SD (Min – max)	Cd (μ g/g) Mean $\pm$ SD (Min – max)	Pb (μ g/g) Mean $\pm$ SD (Min – max)	
Korea (n = 10)	20.89 $\pm$ 3.48 (16.74 – 28.31)	0.98 $\pm$ 0.49 (0.48 – 2.00)	4.41 $\pm$ 0.46 (0.78 – 7.18)	This study
Vietnam (n = 9)	27.23 $\pm$ 6.69 (19.35 – 43.98)	1.10 $\pm$ 0.28 (0.71 – 1.57)	1.60 $\pm$ 1.10 (0.42 – 3.43)	This study
Japan (n = 10)	18.38 $\pm$ 2.60 (15.47 – 22.87)	0.67 $\pm$ 0.13 (0.45 – 0.90)	0.43 $\pm$ 0.17 (0.13 – 0.66)	This study
Indonesia (n = 13)	14.19 $\pm$ 2.77 (10.32 – 18.97)	0.70 $\pm$ 0.13 (0.48 – 0.93)	1.58 $\pm$ 0.90 (0.13 – 14.51)	This study
Taiwan (n = 6)	19.67 $\pm$ 4.11 (16.57 – 27.93)	1.32 $\pm$ 0.57 (0.89 – 2.32)	0.61 $\pm$ 0.14 (0.47 – 0.80)	This study
Thailand (n = 4)	27.80 $\pm$ 1.06 (26.38 – 28.92)	2.48 $\pm$ 0.96 (1.85 – 3.89)	0.98 $\pm$ 0.27 (0.67 – 1.32)	This study
UK (n = 3)	17.72 $\pm$ 1.92 (15.60 – 19.35)	1.96 $\pm$ 0.82 (1.46 – 2.92)	5.60 $\pm$ 0.86 (4.62 – 6.21)	This study
Belgium (n = 3)	23.56 $\pm$ 6.88 (15.81 – 28.94)	1.80 $\pm$ 0.69 (1.29 – 2.58)	8.34 $\pm$ 0.44 (7.86 – 8.73)	This study
Italy (n = 3)	12.37 $\pm$ 0.81 (11.57 – 13.18)	0.65 $\pm$ 0.15 (0.47 – 0.74)	0.48 $\pm$ 0.1 (0.40 – 0.59)	This study
Finland (n = 3)	19.66 $\pm$ 1.58 (17.84 – 20.66)	1.36 $\pm$ 0.18 (1.22 – 1.56)	0.60 $\pm$ 0.03 (0.58 – 0.64)	This study
France (n = 3)	18.01 $\pm$ 1.68 (16.66 – 19.90)	1.68 $\pm$ 0.71 (1.10 – 2.47)	0.69 $\pm$ 0.23 (0.50 – 0.95)	This study
Malaysia	NA	3.05	0.08	(Janaydeh <i>et al.</i> , 2019)
China	NA	0.18	0.64	(Yang <i>et al.</i> , 2005)
USA	(17.9 – 24.9)	NA	NA	(Fresquez <i>et al.</i> , 2015)
Canada	26.8	NA	NA	(Hammond and O'Connor, 2008)
USA	13.0 $\pm$ 1.3	NA	NA	(Panta <i>et al.</i> , 2008)
USA	(20 – 21)	NA	NA	(Swani <i>et al.</i> , 2009)
Poland	(6-74 – 10.56)	NA	NA	(Kowalski and Wiercinski, 2009)
India	< MDL	1.60	0.40	(Dhaware <i>et al.</i> , 2009)
Jordan	NA	2.67	2.64	(Massadeh <i>et al.</i> , 2005)
Saudi Arabia	NA	2.46	1.81	(Ashraf, 2012)
Ireland	NA	(1.73 – 2.02)	(0.38 – 1.16)	(Afridi <i>et al.</i> , 2013)
Pakistan	NA	0.5	14.39	(Ajab <i>et al.</i> , 2008)
Ethiopia	NA	6.07	2.49	(Adam Mekonnen and Bhagwan Singh, 2017)
Iran	NA	2.07	2.71	(Pourkhabbaz and Pourkhabbaz, 2012)
Nigeria	NA	(5.90 – 7.94)	(17.21 – 74.78)	(Benson <i>et al.</i> , 2017)

< MDL: below method detection limit, NA: not available.

co plant is cultivated. This probably explains the significant positive correlations of Hg and Cd with nicotine in the tobacco of cigarettes. Smokers are usually concerned about nicotine concentration in tobacco due to its stimulating nerve effects at different levels. Therefore, this study gives additional information on nicotine concentrations in tobacco of cigarettes due to their harmful effects on human health. The positive correlation may also indi-

cate that the greater the nicotine concentration in tobacco, the higher the Hg and Cd levels, hence the greater the negative health effects on humans. Furthermore, other heavy metals and other tobacco types such as filterless cigarettes, chewing tobacco, and e-cigarettes also need to be studied further.

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Fig. 5. The correlations of nicotine with Hg, Cd, and Pb in the cigarette. (a: correlation between nicotine and Hg, b: correlation between nicotine and Cd, c: correlation between nicotine and Pb).

The absorption ability of Hg, Cd, and Pb by cigarette filter

In this study, Hg, Cd, and Pb concentrations in the filter were found at 0.26 ± 0.24 ng/g cigarette, 0.35 ± 0.25 µg/g cigarette and 0.97 ± 0.92 µg/g cigarette (Table 1). The concentration of Cd remaining in the ash of cigarettes was 0.62 ± 0.42 µg/g cigarette; meanwhile, Pb and Hg were not found ($< \text{MDL}$). The results showed that the concentrations of Hg, Cd, and Pb in filters after smoking were higher than before smoking, indicating that the filter of cigarettes had abilities to absorb Hg, Cd, and Pb from the smoking process.

Basically, the filter of a cigarette is made of cellulose acetate plastic (Ce). In recent days, there are several brands that add activated carbon to the cigarette filter (Ce-C). Therefore, we evaluated the difference of trapping ability between Ce filters (15) and Ce-C filters (14) using 29 cigarettes (Ce: Japan 5, Korea 2, and Vietnam 8; Ce-C: Japan 5, Korea 8, and Vietnam 1). The results of comparison of adsorption (trapping) ability of Hg, Cd, and Pb by the cigarette filter are indicated in Table 3. The metal content of Ce-C (Hg 0.050 ± 0.017 ng/cigarette, Cd 0.010 ± 0.005 µg/cigarette and Pb 0.043 ± 0.017 µg/cigarette) was significantly higher than that of Ce (Hg 0.024 ± 0.013 ng/cigarette, Cd 0.007 ± 0.005 µg/cigarette and Pb 0.018 ± 0.014 µg/cigarette), respectively. After smoking, the metal content of both Ce (Hg 0.044 ± 0.029 ng/cigarette, Cd 0.036 ± 0.017 µg/cigarette and Pb 0.107 ± 0.070 µg/cigarette) and Ce-C (Hg 0.053 ± 0.023 ng/cigarette, Cd 0.062 ± 0.020 µg/cigarette and Pb 0.197 ± 0.114 µg/cigarette) was found to be significant higher compared with before smoking (Ce: Hg 0.024 ± 0.013 ng/cigarette, Cd 0.007 ± 0.005 µg/cigarette and Pb 0.018 ± 0.014 µg/cigarette; Ce-C Hg 0.050 ± 0.017 ng/cigarette, Cd 0.010 ± 0.005 µg/cigarette and Pb 0.043 ± 0.017 µg/cigarette), except for the Hg content of Ce-C. In addition, the metal contents in Ce-C filters after smoking were also found to be higher compared with those of Ce filters, except for Hg. The difference of metal content between Ce-C

Table 3. Metal content in filter (µg/cigarette) and the differences between the means of two groups.

Filter		Hg ng/cigarette	Cd µg/cigarette	Pb µg/cigarette
Ce	A: Before	0.024 ± 0.013	0.007 ± 0.005	0.018 ± 0.014
	C: After	$0.044 \pm 0.029^*$	$0.036 \pm 0.017^*$	$0.107 \pm 0.070^*$
Ce-C	B: Before	$0.050 \pm 0.017^\#$	$0.010 \pm 0.005^\#$	$0.043 \pm 0.017^\#$
	D: After	0.053 ± 0.023	$0.062 \pm 0.020^{*\#}$	$0.197 \pm 0.114^{*\#}$

Ce: Filter that was made of cellulose acetate plastic only. Ce-C: Filter that was made of cellulose acetate plastic with activated carbon added. Data are represented as Mean $\pm$ SD.

*: $P < 0.01$ (A vs C, B vs D), #: $P < 0.01$ (A vs B, C vs D).

and Ce after smoking was identified as Hg 0.009 ng/cigarette, Cd 0.026 µg/cigarette and Pb 0.09 µg/cigarette. Because their levels in cigarettes were evaluated as Hg 12.3 ng/cigarette, Cd 0.94 µg/cigarette and Pb 1.62 µg/cigarette, the ratio of trapped metals by filter was estimated as Hg 0.07%, Cd 2.77% and Pb 5.56%. Meanwhile, the trapping ratio of Ce-C (Cd: 5.53%, Pb: 5.41%) was higher than that of Ce (Cd: 3.09%, Pb: 5.49%). On the other hand, Hg had lower absorption in both types of filters (Ce: 0.15%, Ce-C: 0.02%). Even though Ce-C has relatively higher trapping ability compared with Ce, both filters did not have enough trapping ability for metals, especially Hg.

As far as the authors know, this experiment was the first of its kind to be performed regarding Hg. As for Cd and Pb, although Ziarati *et al.* (2017) published that the ratios of Cd and Pb absorbed and trapped by filter were 116-234% and 112-198%, the report did not show the detailed information. Therefore, it was difficult to understand the absorbing abilities of Cd and Pb from tobacco of cigarettes to smoke. From the results of this study, the authors considered that the filters could not absorb Cd, Pb and Hg effectively. The experiment showed that Pb and Hg were not found in ash except that Cd remained at a small concentration (0.62 ± 0.42 µg/g) in the ash. Therefore, almost all Cd, Pb, and Hg from tobacco and rolling paper also flowed with smoke when smoking. When a cigarette is smoked, the temperature in the cigarette's tip reaches a high value (up to 950°C) (World Health Organization, 2019); at such a temperature, Cd, Pb, and Hg easily vaporize and become swept into a stream by smoke. Hg in particular easily vaporizes at high temperatures and this may explain why Hg absorption ability was the lowest. In Pb and Cd's case, as we know, Pb has a density (11.3 g/cm³) higher than that of Cd (8.65 g/cm³). That is perhaps the reason Pb was absorbed more effectively than Cd in the filter of cigarettes. In the designed experiment, the pump was kept running non-stop to keep all smoke flowing through the filter. Therefore, cigarette smoke contains harmful substances such as heavy metals that go to mainstream smoke. In fact, when humans smoke, the smoke of cigarettes separately becomes two flows that are mainstream and side-stream; meanwhile, both affect the active smoker and passive smoker in different levels that belong to smoking frequency and types of tobacco.

In conclusion, this study provides a comprehensive survey of Hg, Cd, and Pb in marketed cigarettes collected from Korea, Vietnam, Japan, Indonesia, Taiwan, Thailand, the UK, Belgium, Italy, Finland, and France with an objective assessment on an international scale. Accord-

ing to the authors, this is the first research on the distribution concentration of Hg, Cd, and Pb in three parts of cigarettes separately: filter, tobacco, and rolling paper. One of the new findings of this research was that a significant correlation between Hg and Cd was found; and there is no correlation between each of these heavy metals and Pb. In addition, the nicotine in cigarettes showed a significant positive correlation with Cd and Hg. Even the lower metal trapping efficacy of active carbon additive filters was relatively higher as compared to those without active carbon, indicating the addition of activated carbon to the filter contributes to a minimal extent to the health of smokers. Notably, the ability to absorb Hg was not significantly different between these types of filters. The novelty of this study's key point was we found in the fact that the cigarette filter could not absorb Cd, Pb, and Hg well.

This study provides valuable data and information on Hg, Cd, and Pb in marketed cigarettes for tobacco companies, public health protection agencies, public health environment organizations, and the general smoking population concerning the effect of Hg, Cd, and Pb in marketed cigarettes.

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Conflict of interest---- The authors declare that there is no conflict of interest.

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