The Content of Heavy Metals in Cigarettes and the Impact of Their Leachates on the Aquatic Ecosystem

Maria Michael 1,†, Arun Meyyazhagan 1,‡, Krishnakumar Velayudhannair 1,* , Manikantan Pappuswamy 1,©, Anu Maria 1, Vincent Xavier 1, Balamuralikrishnan Balasubramanian 2,©, Rathinasamy Baskaran 3,©, Hesam Kamyab 4,5,*©, Yasser Vasseghian 6,©, Shreeshivadasan Chelliapan 7,©, Maryam Safa 8, Zohre Moradi 9 and Mohamed Amine Khadimallah 10,11

1 Department of Life Sciences, Bangalore Central Campus, CHRIST University, Hosur Road, Bengaluru 560029, India; maria.michael99@gmail.com (M.M.); arun47biotech@gmail.com (A.M.); manikantan.p@christuniversity.in (M.P.); anumariyamadukkakuzhiyil@gmail.com (A.M.); xavier.vincent@christuniversity.in (V.X.)
2 Department of Food Science and Biotechnology, College of Life Science, Sejong University, Seoul 05006, Korea; bala.m.k@sejong.ac.kr
3 Department of Bioinformatics and Medical Engineering, Asia University, Taichung 41354, Taiwan; baskaran@asia.edu.tw
4 Malaysia-Japan International Institute of Technology, Universiti Teknologi Malaysia, Jalan Sultan Yahya Petra, Kuala Lumpur 54100, Malaysia
5 Department of Biomaterials, Saveetha Dental College and Hospital, Saveetha Institute of Medical and Technical Sciences, Chennai 600077, India
6 Department of Chemistry, Soongsil University, Seoul 06978, Korea; vasseghian@ssu.ac.kr
7 Engineering Department, Razak Faculty of Technology & Informatics, Universiti Teknologi Malaysia, Jalan Sultan Yahya Petra, Kuala Lumpur 54100, Malaysia; shreeshivadasan.kl@utm.my
8 Institute of Research and Development, Duy Tan University, Da Nang 550000, Vietnam; maryamsafa@duytan.edu.vn
9 Department of Electrical Engineering, Faculty of Engineering and Technology, Imam Khomeini International University, Qazvin 34149-16818, Iran; z.moradi@edu.ikiu.ac.ir
10 Department of Civil Engineering, College of Engineering, Prince Sattam bin Abdulaziz University, Alkhair 16273, Saudi Arabia; m.khadimallah@psau.edu.sa
11 Laboratory of Systems and Applied Mechanics, Polytechnic School of Tunisia, University of Carthage, Tunis 1054, Tunisia
* Correspondence: krishnakumar.v@christuniversity.in (K.V.); hesam_kamyab@yahoo.com (H.K.)
† These authors contributed equally to this work.

Abstract: Smoked cigarettes and butts are the most common kind of litter around the world. The buildup of these litters has badly polluted local water bodies and their compartments, and the cumulative effect of many cigarette butts scattered in a centralized location may pose a serious hazard to living species. To understand how heavy metals are leached out into the aquatic ecosystem, researchers must analyse the behavior of the materials that make up cigarettes. Using atomic absorption spectrometry, this study evaluated the content of several metals (such as Cd, Cu, Fe, Pb, Sn, Zn, and Hg) leached from various brands of unsmoked and smoked cigarettes and cigarette butts. The findings revealed that heavy metal is more prevalent in butte. These findings indicate that cigarette litter is a major source of metal contamination in the aquatic ecosystem and that apparent leaching may increase the risk of toxicity to aquatic organisms.

Keywords: aquatic pollution; ecotoxicology; risk assessment; monitoring; toxicology

1. Introduction

Smoked cigarettes and their butts constitute the most common form of litter worldwide to which people can be exposed [1,2] and one of the largest wastes generated in our society [3]. Local water bodies and their compartments have been severely polluted by the
accumulation of this litter [4], and the cumulative effect of many cigarette butts littered in a centralized area may present a significant threat to living organisms [5,6].

There are two types of cigarette smoking: mainstream smoking (MSS) and side stream smoking (SSS). Several studies say that SSS, in which the smoke is released from the tip of the cigarette, contains higher levels of a cancer-causing substance [6]. The heavy metals and trace elements present in the cigarette butt leachates are the reason for the toxicity in the organisms [6]. Although the presence of various compounds in cigarettes and their butts has been extensively studied, few reports are available on the amount of these components leached into the aquatic medium [6,7]. The occurrence of heavy metals in cigarettes is largely due to the soil condition where the tobacco (*Nicotiana tabacum*) is being cultivated [8,9]. Apart from that, the application of pesticides, insecticides, and herbicides, the addition of casing materials to the tobacco leaf [10], cured leaves [11,12], and the use of brightening agents on the wrapping paper [13–16]. Most of the chemicals produce new compounds when the tobacco is burned [17,18].

The response of aquatic biota to the accumulation of various heavy metals in the waterbodies and the physical parameters, such as pH [19], to heavy metal contamination are highly varied [19,20]. Hence, it is essential to study the leaching behavior of cigarettes to understand how the heavy metals are leached out into the aquatic ecosystem. In this context, the present study aims to determine the concentration of different metals such as Cd, Cu, Fe, Pb, Sn, Zn, and Hg leached from the different brands of unsmoked and smoked cigarette and cigarette butts in an aqueous solution and to assess the concentration of the leached metals as regards the soaking time of the cigarette samples. The selection of the above metals for the study is based on their presence in smoked filters [21–23] and their toxicity to living organisms [24].

2. Materials and Methods

2.1. Sampling of Cigarettes

Packs of the three most popular tobacco cigarette brands produced in India were purchased from local shops in Bengaluru, South India. Following collection, the filters and tobacco portions of the cigarettes were cut and separated manually. Cigarettes from each brand were sampled as unsmoked cigarette (USC), smoked cigarette (SC), unsmoked butt (USB), and smoked butt (SB) (Figure 1). To avoid contamination and moistening caused by humidity in the laboratory, all these samples were stored separately in disposable plastic containers.

- **Unsmoked cigarette (USC):** The cigarettes were cut, without smoking, at a third of the way up the cigarette using a sterile scissor, and the remaining portion (including tobacco and butt) was sampled as USC.
- **Smoked Cigarette (SC):** Cigarettes were smoked artificially until half of the cigarette (1/3 from the top) was sampled as SC.
- **Unsmoked Butt (USB):** The cigarette’s filter (butt) was cut and removed before being sampled as USB.
- **Smoked Butt (SB):** Cigarettes were smoked artificially until the butt was exposed and sampled as SB.
2.2. Smoking of Cigarettes

According to Micevska et al. [6], the cigarettes were smoked artificially. In a nutshell, five cigarettes from three different brands were smoked separately by placing a lit cigarette against a vacuum and using a plastic bottle filled with water that had been fitted with an outlet at its back end (Figure 2).

The on and off outlet of water helps in mimicking the action of a smoker [6]. The cigarettes were smoked down from the top as mentioned in the previous section.
2.3. Preparation of Leachates

Separate leachates of all four samples (USB, SB, USC, and SC) from three different brands were prepared by adding them to phials of an aqueous solution. All of the samples (USC, SC, USB, and SB) were immersed in aqueous solutions for 24 h. For each sample, five duplicates were taken. A blank was also prepared in the same way, but without any cigarette material [5]. Figure 3 depicts a summary of this procedure.

![Figure 3. Schematic diagram of samples (leachate) used for the present study.](image)

2.4. Heavy Metal Analysis in Cigarette Samples

Eneji et al. [25] methods were used to analyse heavy metals present in various cigarette brand samples. All of the samples were cut into tiny pieces with scissors and washed in 4 mL of 1 percent HNO₃. A crucible was used to place the samples in a muffle furnace. For one hour, the muffle furnace was set to 5000 °C. Water was used to moisten the ignited residues. Five mL of 4N HCl was carefully added to this, and the mixture was filtered through Whatman filter paper into a 50 mL volumetric flask. This was diluted to the appropriate concentration and stored at 40 °C for analysis using atomic absorption spectroscopy (AAS model AA-6880, Shimadzu, Japan), with a measurement range of 185–900 nm, photomultiplier tube detector, flame type.

2.5. Acid Digestion of Cigarette Leachates

Fifty mL of leachate were prepared per sample and were subjected to acid digestion using concentrated H₂SO₄ and concentrated HNO₃. All glassware and containers used for the process of acid digestion were washed with 1% HNO₃ before the treatment. To the sample, 0.5 mL of concentrated H₂SO₄ and 1 mL of concentrated HNO₃ were added and were incubated for 4 h in a boiling water bath [26]. After completion of the four hours, the digested samples were filtered into a 50 mL volumetric flask using Whatman filter paper. The solution was diluted to 50 mL using distilled water and stored at 4 °C for further analysis using atomic absorption spectroscopy (Model AA-6880, Shimadzu, Japan).
2.6. Statistical Analysis

All of the data were statistically analysed. For the statistical analysis, SPSS Version 20 (IBM®, Armonk, NY, USA) was used. The tools, such as standard deviation and mean, were discovered for all of the samples, and significant variation was discovered using a graph.

3. Results

The levels of various heavy metals, such as Cd, Cu, Fe, Pb, Sn, Hg, and Zn, present in three different popular brands of Indian cigarettes sold in Bengaluru, South India, were analysed in this study. To facilitate understanding, the cigarette brands were classified as expensive, moderate, or cheap based on their selling price. Each brand includes four samples: an unsmoked cigarette (USC), a smoked cigarette (SC), an unsmoked butt (USB), and a smoked butt (USB) (SB). Heavy metals found in these samples (direct and leachate) were investigated.

3.1. Content of Heavy Metals in the Different Samples of Expensive Brand

The highest level of Cd was found in SB (0.52 ± 0.01 µg/g) and the lowest level was found in USC and USB (0.25 ± 0.03 and 0.24 ± 0.02 µg/g, respectively). According to statistical analysis, the difference in Cd levels between SB and other samples is significant ($p < 0.05$), whereas the difference between SC, USB, and USC is insignificant ($p > 0.05$). The USB and SC samples had the highest levels of Cu (151.30 ± 5.76 and 162.94 ± 6.80 µg/g, respectively), while the SC and USC samples had the lowest levels of Cu (73.79 ± 0.36 and 86.61 ± 0.91 µg/g, respectively). The statistical analysis revealed that there is a significant difference ($p < 0.05$) between butts and cigarettes, but not between USB and SB or USC and SC ($p > 0.05$). Iron (Fe) content was found to be highest in USC (105.48 ± 0.39 µg/g), followed by SC and USB (87.93 ± 3.56 and 51.15 ± 2.04 µg/g, respectively). The statistical analysis revealed that there is a statistically significant difference ($p < 0.05$) between the four samples. The highest lead (Pb) content was found in SB (19.86 ± 2.39 µg/g), followed by USB and SC (16.97 ± 1.46 and 12.44 ± 1.40 µg/g, respectively). The USC has the lowest level of Pb (9.97 ± 0.49 µg/g). The statistical analysis of the Pb levels in the samples revealed a significant difference ($p < 0.05$). SB (869.05 ± 19.11 µg/g) had the highest tin (Sn) content, followed by USB and SC. USC has the lowest level of Sn, with an insignificant difference, followed by SC (599.60 ± 15.98 and 466.88 ± 8.33 µg/g, respectively). It was discovered that USC had the lowest content of Sn (438.32 ± 2.89 µg/g). The statistical analysis of the level of Sn between the samples revealed a significant difference ($p < 0.05$). The content of zinc (Zn) in USB was found to be high (45.21 ± 1.48 g/g), whereas the level of Zn in SC was found to be low (24.40 ± 0.71 µg/g). The sample USC (305.34 ± 8.14 µg/g) contained a high amount of Hg, whereas the sample SC contained the least amount of Hg (104.78 ± 3.08 µg/g), indicating a significant difference ($p < 0.05$) (Figure 4).
3.2. Levels of Heavy Metals in Different Samples of a Moderate Brand

Cd content was found to be high in samples SB and USB (1.18 ± 0.08, 1.15 ± 0.07 µg/g, respectively), while Cd content was lowest in USC and SC (0.56 ± 0.01, 0.55 ± 0.08 µg/g, respectively). The difference in Cd content between butts and cigarettes is significant (p < 0.05), whereas the difference between SB and USB and USC and SC is insignificant (p > 0.05). The USB had the highest level of Cu (287.53 ± 043.29 µg/g), followed by the SB (185.35 ± 15.00 µg/g), while the samples SC and USC had the lowest levels of Cu (96.85 ± 6.04 and 105.07 ± 8.51 µg/g, respectively). Iron (Fe) levels were found to be high in the SB (24.42 ± 1.18 µg/g) and lowest in SB (2.76 ± 0.10 µg/g), but samples of USC and SC (14.14 ± 1.07 and 12.70 ± 1.68 µg/g) had similar values with an insignificant difference (p > 0.05). The statistical analysis of the Pb levels in the samples revealed a significant difference (p < 0.05). The content of tin (Sn) showed the highest trend in USB and SB (1184.51 ± 10.82 and 1168.60 ± 15.39 µg/g, respectively), with an insignificant difference (p > 0.05), whereas USC and SC registered low levels for Sn (617.69 ± 17.20 and 567.61 ± 11.69 µg/g, respectively), with an insignificant difference (p > 0.05). The content of tin (Sn) showed the highest trend in USB and SB (1184.51 ± 10.82 and 1168.60 ± 15.39 µg/g, respectively), with an insignificant difference (p > 0.05), whereas USC and SC registered low levels for Sn (617.69 ± 17.20 and 567.61 ± 11.69 µg/g, respectively), with an insignificant difference (p > 0.05). The content of zinc (Zn) in USB was found to be high (141.92 ± 9.57 µg/g), while the level of Zn in SC was found to be low (37.10 ± 6.79 µg/g). The samples SB and USB had a high amount of Hg (359.02 ± 19.05 and 331.38 ± 8.09 µg/g, respectively), while USC and SC had a lower amount of Hg (140.87 ± 4.36 µg/g and 158.36 ± 5.75 µg/g), with an insignificant difference (p > 0.05) (Figure 5).
3.3. Levels of Heavy Metals in the Different Samples of Cheap Brand

Cd content was found to be high in the samples USC and SB (0.12 ± 0.02 and 0.13 ± 0.01 µg/g, respectively), while the lowest levels were found in the samples USB and SC (0.05 ± 0.0 and 0.07 ± 0.02 µg/g respectively). According to statistical analysis, the difference in Cd levels between USC, SB, and between USB, SC is significant (p < 0.05), whereas the differences between USC and SB and between USB and SC are insignificant (p > 0.05). The USB sample had the highest level of Cu (148.0 ± 0.71 µg/g), followed by the SB (117.94 ± 1.02 µg/g), while the samples USC and SC had nearly identical values (165.33 ± 3.45 and 161.49 ± 4.61 µg/g, respectively). Iron (Fe) levels were found to be high in USB (232.88 ± 13.16 µg/g), followed by the SB (203.82 ± 12.34 µg/g). The samples USC and SC had nearly identical values (165.33 ± 3.45 and 161.49 ± 4.61 μg/g, respectively). According to statistical analysis, the differences between USC and SB and between USB and SC are insignificant (p > 0.05). The levels of Hg were found to be high in USB (205.11 ± 9.62 µg/g), followed by SB and USC (141.25 ± 6.23 and 101.34 ± 4.57 µg/g respectively). Statistical analysis revealed that the difference between butts and cigarettes is significant (p < 0.05) but the difference between samples USC and SC is insignificant. The highest level of lead (Pb) was found in USB (15.84 ± 2.37 µg/g), followed by SB and USC (13.69 ± 1.67 and 8.90 ± 1.66 µg/g, respectively) and USC (5.77 ± 1.33 µg/g). The statistical analysis of the Pb levels in the samples revealed a significant difference (p < 0.05). In all of the samples, Sn was found to be undetectable or absent. The level of zinc (Zn) was found to be high in USB and SB (39.37 ± 3.43 and 40.93 ± 2.00 µg/g) while the lowest level of Zn was found in USC and SC (29.36 ± 3.03 and 31.89 ± 3.44 µg/g). Statistical analysis revealed a significant difference between butts and cigarettes (p < 0.05), whereas the difference between USB, SB, USC, and SC was insignificant (p > 0.05). The levels of Hg were found to be high in USB (205.11 ± 9.62 µg/g), followed by SB and USC (141.25 ± 6.23 and 101.34 ± 4.57 µg/g respectively). The lowest level of Hg was found to be in SC (76.66 ± 0.74 µg/g). Statistical analysis revealed that there is a significant difference between the different samples (Figure 6).
3.4. Levels of Heavy Metals in the Leachates of Different Samples of an Expensive Brand

Cd levels in USB (0.38 ± 0.01 g/g) were found to be high, followed by USC (0.11 ± 0.0 µg/g). The Cd levels in SB and SC were discovered to be the same (0.02 ± 0.0 µg/g and 0.02 ± 0.02 µg/g, respectively). The statistical analysis of Cd reveals a significant difference (p < 0.05) between the levels of USB, USC, and the other samples. Cd levels were found to be insignificantly different between samples SB and SC (p > 0.05). Among the four samples, USB had the highest concentration of Cu (40.15 ± 1.83 µg/g), while SC had the lowest (13.45 ± 11.09 µg/g). The samples of USC and SB registered with almost similar values (24.57 ± 3.25, 23.16 ± 2.15 µg/g, respectively). Statistical analysis reveals that there is a significant difference between USB and SC (p < 0.05), whereas the difference in Cu levels between USC and SB is insignificant (p > 0.05). Iron (Fe) levels were found to be high in USB and SB (125.75 ± 9.01 and 117.66 ± 3.46 µg/g, respectively), followed by USC (73.62 ± 0.50 µg/g). SC contained the least amount of Fe (17.55 ± 13.20 µg/g). Statistical analysis reveals a significant difference (P < 0.05) between butts and cigarettes. The difference in Fe levels between USB and SB was found to be insignificant (p > 0.05), whereas the difference between USC and SC was found to be significant (p < 0.05). Lead (Pb) levels were found to be highest in USB (29.25 ± 3.51 µg/g), followed by SB, USC, and SC (6.38 ± 1.08, 5.51 ± 0.41, and 2.181.50 µg/g, respectively). Statistical analysis reveals a significant difference between all four samples (p < 0.05). In all four samples, the level of Sn was found to be below the detectable level. Among the four samples, USB and SB had high levels of Zn (31.87 ± 0.54 and 33.0 ± 2.12 µg/g, respectively), whereas USC and SC had low levels of Zn (17.29 ± 0.19 and 11.30 ± 7.99 µg/g, respectively). Statistical analysis reveals a significant difference in Zn levels between butts and cigarettes (p < 0.05), whereas the difference between samples was found to be insignificant between USB and SB and between USC and SC (p > 0.05) (Figure 7).
3.5. Levels of Heavy Metals in the Leachates of Different Samples of the Moderate Brand

The level of Cd in the sample USB was found to be high (0.89 ± 0.02 µg/g), followed by SC (0.12 ± 0.02 µg/g). Cd levels in the samples USC and SB were the same (0.05 ± 0.0 g/g). Statistical analysis reveals that the difference in Cd levels between USB and SC is statistically significant (p < 0.05). Among the four samples, the USB had the highest level of Cu (89.15 ± 3.77 µg/g), followed by the USC (25.85 ± 1.08 µg/g), and the SC and SB had the lowest levels of Cu (11.69 ± 0.73 and 11.13 ± 0.26 µg/g, respectively). Iron (Fe) levels were found to be high in SB and USB (246.37 ± 2.99 and 242.8 ± 10.59 µg/g, respectively), followed by USC (124.58 ± 5.81 µg/g). SC had the lowest level of Cu (105.11 ± 3.45 µg/g). The statistical analysis revealed an insignificant difference between the samples SB and USB (p > 0.05), but a significant difference in Cu levels between butts and cigarettes (p < 0.05). The highest lead (Pb) concentration was found in USB (128.89 ± 8.53 g/g), followed by SC and SB (21.25 ± 1.32 and 16.29 ± 0.48 µg/g, respectively). USC had the lowest Pb concentration (5.88 ± 0.36 µg/g). The statistical analysis of the Pb levels in the samples revealed a significant difference. USC had the highest trend in tin (Sn) levels (3.64 ± 0.55 µg/g). In the samples USB, SB, and SC, the level of Sn was below the detectable range. The zinc (Zn) content of USB was found to be high (64.00 ± 9.28 µg/g), followed by SB (40.96 ± 0.54 µg/g). The levels of Zn in the samples USC and SC were comparable (27.74 ± 1.14 and 25.95 ± 1.36 µg/g, respectively). Statistical analysis of Zn levels revealed a significant difference between butts and cigarettes, as well as between USB and SB (P0.05), but no significant difference between USC and SC (p > 0.05) (Figure 8).
3.6. Levels of Heavy Metals in the Leachates of Different Samples of the Cheaper Brand

Cd levels were found to be similar in all three samples USB, SB, and SC, but significantly lower in USC. The statistical analysis reveals that the levels of Cd in the four samples (USB, SB, and SC) differ insignificantly ($p > 0.05$). The USB sample had the highest level of Cu ($89.76 \pm 0.08 \mu g/g$), followed by the SC and USC ($12.05 \pm 0.47$ and $10.29 \pm 0.50 \mu g/g$, respectively). The level of Cu in sample SB was below the detectable level. According to the statistical analysis, there is a significant difference between butts and cigarettes. Cu levels in SC and USC samples were insignificantly different. Iron (Fe) levels were found to be high in the USB ($769.36 \pm 17.02 \mu g/g$), followed by the USC and SB ($191.47 \pm 8.41$ and $107.62 \pm 0.80 \mu g/g$, respectively). SC contained the least amount of Fe ($66.47 \pm 2.12 \mu g/g$). The level of Fe in all four samples differs significantly, according to statistical analysis. The highest level of lead (Pb) was found in SC ($18.06 \pm 1.41 \mu g/g$), followed by USB and USC ($9.68 \pm 0.66$ and $2.61 \pm 0.29 \mu g/g$, respectively). The SB sample had the lowest level of Pb ($0.83 \pm 0.80 \mu g/g$), and statistical analysis shows that there is a significant difference between all four samples ($p < 0.05$). Among the four samples, USB and SB contained a high level of Sn ($168.60 \pm 9.40$ and $153.93 \pm 7.02 \mu g/g$, respectively), whereas USC and SC contained a lower level of Sn ($106.60 \pm 2.50$ and $103.16 \pm 0.68 \mu g/g$, respectively). Butts and cigarettes have a statistically significant difference. The difference in Sn levels between samples USB and SB was found to be insignificant ($p > 0.05$) (Figure 9).
were generally higher than those in leachates prepared from cigarettes. This difference could be attributed to heavy metal loss in smoke or ash during cigarette combustion [35,36]. However, Hg and Sn were not found in the leachate, despite the presence of these metals in the cigarettes. Similar findings were made with Hg [33,34]. However, the Fe [21,28] and Cd [21,27] content reported in the present study was relatively lower. This could be due to differences in leaching methods and the number of samples used.

When comparing the present study to previous studies, the mean of lead (Pb) was found to be highest among the samples analysed in the current study. The mean amount was found to be 16.85 g/g, with a minimum of 0.834 g/g and a maximum of 128.893 g/g, and the amount was found to be higher in the cigarette leachates. This was significantly higher than other reports [27–32]. The current study found a mean of 78.98 g/g of copper with a maximum of 287.52 g/g, which was several times higher than previous reports [28,29]. Similar findings were made with Hg [33,34]. However, the Fe [21,28] and Cd [21,27] content reported in the present study was relatively lower. This could be due to differences in leaching methods and the number of samples used.

The current study investigated leachates of unsmoked cigarettes and butts to provide concentrations of the metals of interest leached out into the environment and to identify possible instances of contamination. Metal concentrations in leachates prepared from butts were generally higher than those in leachates prepared from cigarettes. This difference could be attributed to heavy metal loss in smoke or ash during cigarette combustion [35,36]. However, Hg and Sn were not found in the leachate, despite the presence of these metals in the cigarettes. Metal concentrations in cigarettes may vary between brands. The relative percentage of the mean value with a standard deviation of heavy metal present and leached is relatively low for most sample sets, demonstrating the method’s reproducibility. The leaching procedure used in this preliminary study is not an open system geared toward mimicking the natural environment; a closed system is the simplest way to obtain the maximum amount of leachable metal. Another limitation of this research is the lack of information on the interactions of various other physicochemical parameters such as pH, temperature, and so on.

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In this study, smoked cigarette material and butts were collected due to their popularity and used to provide a sample population representative of local cigarette litter in terms of the brand and amount of remnant tobacco, but metal concentrations in cigarettes may vary between brands. The relative percentage of the mean value with a standard deviation of heavy metal present and leached is relatively low for most sample sets, demonstrating the method’s reproducibility. The leaching procedure used in this preliminary study is not an open system geared toward mimicking the natural environment; a closed system is the simplest way to obtain the maximum amount of leachable metal. Another limitation of this research is the lack of information on the interactions of various other physicochemical parameters such as pH, temperature, and so on.

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**Figure 9.** Level of heavy metals in different leachate samples of the cheaper brand.

4. Discussion

Cigarettes are found littered everywhere, posing a serious threat to the environment. The present study attempted to determine the level of various heavy metals present in popular cigarette brands sold in Bengaluru, South India, as well as the amount of heavy metals leached out into the aquatic medium. Popular tobacco cigarette brands were used for this purpose. Cadmium, copper, tin, lead, iron, mercury, and zinc were all tested in the samples. Cigarette litter—both smoked cigarettes and butts—thrown into the environment include a wide variety of cigarette brands with varying amounts of tobacco left on the filters.

In this study, smoked cigarette material and butts were collected due to their popularity and used to provide a sample population representative of local cigarette litter in terms of the brand and amount of remnant tobacco, but metal concentrations in cigarettes may vary between brands. The relative percentage of the mean value with a standard deviation of heavy metal present and leached is relatively low for most sample sets, demonstrating the method’s reproducibility. The leaching procedure used in this preliminary study is not an open system geared toward mimicking the natural environment; a closed system is the simplest way to obtain the maximum amount of leachable metal. Another limitation of this research is the lack of information on the interactions of various other physicochemical parameters such as pH, temperature, and so on.

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might leach. Rapid metal release may have acute biological consequences for local aquatic organisms sensitive to Pb, Cd, and Zn. The findings of this study also revealed that metal concentrations leached from unsmoked cigarettes were higher in general than in smoked cigarette materials. This implies that cigarette litter containing more remnant tobacco is more likely to cause contamination than butts containing little or no remnant tobacco. This finding calls into question a practice by some environmentally conscious smokers of scattering remnant tobacco into the environment but keeping the filter until it can be deposited in a waste container.

5. Conclusions

We compared the content of heavy metals present and leached into the aquatic ecosystem from both cigarettes and butts. The findings revealed that the butts of both smoked and unsmoked samples (SB and USB) contain more heavy metals than the tobacco part of a cigarette and that they release a relatively higher concentration of heavy metals into the aquatic ecosystem. Furthermore, the apparent rapid leaching of heavy metals from littered cigarette and butt samples raises the possibility of acute toxicity to aquatic life. As a result, additional research is needed to determine the impact of heavy metals leached from littered cigarette butts on aquatic life and the environment in general.

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