Determining cadmium levels in herbal tooth powders purchased from streetmarkets in Lahore, Pakistan

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Abstract
The present study was designed to determine the concentration of Cadmium(Cd) in herbal tooth powders purchased from street markets in Lahore using Atomic Absorption Spectrophotometer. The concentrations of Cd in 15 samples of herbal tooth powders were determined and compared with the permissible limit established by the Food and Agriculture Organization and World Health Organization. The concentrations of Cd in 3 herbal toothpaste samples were also determine to compare with herbal tooth powders during the present study. The samples of herbal tooth powders were subjected to an acid digestion with HNO₃ and HClO₄ and the concentration of Cd in samples was determined AAS. Cadmium was detected in 8 samples. None was detected (ND) in 7 samples. Cd levels ranged between 0 ppm (ND) and 1.392 ppm in different herbal powders. The average concentration of Cd in different tooth powdered products was 0.30 ppm, while in herbal toothpastes it was 0.7919 ppm. The concentrations of Cd in most of the samples under study were within the permissible limit approved by FAO/WHO (0.3 ppm). The results showed that most of the herbal tooth powders from various local markets in Lahore (72%) have low concentrations of Cd and do not pose any serious health risks to consumers. The present research emphasizes on the importance of establishing national permissible limits for different heavy metals for herbal products in Pakistan.

Keywords: Atomic absorption spectrophotometer; cadmium; FAO/WHO; herbal tooth powders and permissible limits.

1. Introduction
Cadmium (Cd) is a soft, silver-white metal in group IIb of the periodic table. Its melting point is 320.9°C, while its boiling point is 765°C. When present in air, cadmium is oxidized into cadmium oxide. Because cadmium is toxic to humans and animals, it is a health threat. Heavy metals are naturally found in combination with other minerals. Cadmium is usually found with Zinc, Lead and Copper.

Heavy metals are harmful and poisonous to humans due to their high specific gravity. Cadmium is well-known as a toxic heavy metal which can have damaging effects on human organ systems, including carcinogenic effects. Unfortunately, cadmium’s production and environmental release have increased due to human activities (Mahmood et al., 2012; Zinsaza, 2015). In addition, it can accumulate in humans. Its main sources are cigarette smoke, welding, impure food and drinks. Human exposure to cadmium can occur from the intake of polluted food or water. As a result, humans can have prolonged negative health impacts. Other sources of contamination can be impure drugs and dietary supplements (Bernhøft, 2012).

Cadmium is also present in the environment, so humans can be exposed to it in their occupational settings especially chemical manufacturing industries. If cadmium is absorbed in the body, it can remain there and build-up over time. Cadmium mainly accumulates in the liver and kidneys, where it is is toxic to proximal tubular cells. Chronic kidney dysfunction can occur with high Cd-concentrations. Cell injury and cell death can be caused by cadmium if it prevents calcium circulation in the body. Also, bone demineralization can be caused by cadmium, leading to direct or indirect bone damage due to renal dysfunction (Bernard, 2008; Musa and Abdullahi, 2013).

The use of herbs and herbal products for medicinal purposes is called herbalism. Throughout history, humans have managed their health by using herbs for medicinal purposes. Ancient people used different parts of plants, animals and several minerals to cure different ailments. The parts of plants or plant extracts present in herbal medicines work together to cure the ailments. Herbal products can be made from any part of the plant but
mainly from roots, leaves, flowers and bark. Such herbal products are ingested, inhaled, drunk or directly applied to the skin. Plants naturally contain biochemical ingredients which become part of herbal products and provide therapeutic assistance (Kunle et al., 2012). In order to reduce environmental exposure of cadmium, actions must be taken at national, regional and global levels (Zinsaza et al., 2015).

Toothpaste and other tooth care products are used daily in order to maintain dental hygiene. Commercial name-brand toothpastes are the most common, herbal toothpastes are becoming more popular. These contain ingredients sourced from plants and plant extracts such as peppermint, sage, thyme, aloe vera, eucalyptus and basil leaf extracts. As these ingredients are sourced from the environment, it is possible that they have heavy metals contaminants. Heavy metals are harmful and poisonous to humans due to their high specific gravity. Because heavy metals exist naturally in the environment in rocks and soil, plants absorb them directly or indirectly. These plants could be cultivated for the preparation of herbal products (Adogu et al., 2015).

Most herbal products are composed of active pharmacological components in addition to several trace metals and minerals (Yuan et al., 2016). Different conventional medicinal systems make use of herbal plants, and recently these systems have expanded in the primary health care arbitration throughout the world. According to the World Health Organization (WHO, 2010), traditional medicines made from herbal plants are the primary remedies for almost 70-80% of the world’s population. For example, Herbs are commonly used for the treatment and prevention of illnesses such as headache, rheumatism, stomachache, hypertension, diabetes and others (Sakkir et al., 2012).

The present study aims to determine the concentration of cadmium in different herbal tooth powders available in the markets of Lahore, Pakistan. The goal was to evaluate their relative safety and potential health effects based on the Food and Agriculture Organization and World Health Organization’s permissible limits (FAO/WHO, 2006).

2. Materials and methods

A total of 18 samples of herbal tooth care products were purchased from street markets of Lahore, Pakistan to determination cadmium concentrations. The samples included 15 powdered and 3 toothpaste samples. The study was conducted over a 5-month period from February to June 2016.

Lab work was carried out in the Environmental Sciences Research Laboratory of Lahore College for Women University.

2.1. Materials

Nitric acid (65%) and perchloric acid (30%) were used as reagents for the wet digestion of samples. Solutions were prepared in three different concentrations (1mg/L, 2mg/L and 3mg/L) in order to obtain a calibration curve by diluting a stock solution of 1000.

2.2. Method for analysis of powdered samples

To begin, 1g/1ml of sample was taken in a beaker. 10mL of concentrated nitric acid (65%) were added and left overnight at room temperature. After 24 hours, 4mL of the perchloric acid (30%) were added to the sample and concentrated on a hotplate at 60°C so that approximately 1mL of suspension remained in the beaker. The suspension was cooled and diluted with deionized water. The resulting solution was then filtered. Solutions were then added into test tubes. For comparison of Cd concentration in herbal tooth powders, 3 locally available herbal toothpastes were also analyzed.

2.3. Method for herbal toothpastes

For each sample, around 2g of toothpaste were weighed in 150ml conical flasks. Five ml of water and 5ml HNO₃ were added to each flask, and the solutions were stirred until the toothpastes dissolved at low heat. Each of the solutions was cooled. Thereafter, 1.5ml of the 30% HClO₄ solution were added to each flask and then stirred. The pH was adjusted at 1.1-1.2 with the 1% NH₄OH solution. After that, the sample solutions were filtered. Solutions were then added into test tubes and analyzed by atomic absorption spectrophotometer.

3. Results

The cadmium analysis results for the selected samples are shown in Figure 1 and compared to the FAO/WHO permissible limits. Five samples (three toothpastes and two powdered samples) showed high amounts as compared to other samples and the WHO limits. These were deemed to pose some health risks.
Thirteen samples of herbal powders had Cd concentrations below FAO/WHO permissible limits. Seven of the powders did not have any detectable amounts of Cd, while six samples had very low Cd-concentrations when compared to the WHO standard value (0.3 ppm).

**Fig. 1.** Concentration of Cd (ppm) in different herbal tooth care products in comparison to FAO/WHO permissible limit.

**Table 1.** Sample ID and concentration of cadmium in all the samples in ppm. (ND = not detected)

<table>
<thead>
<tr>
<th>No. of samples</th>
<th>Sample ID</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P1</td>
<td>0.3039</td>
</tr>
<tr>
<td>2</td>
<td>P2</td>
<td>0.0037</td>
</tr>
<tr>
<td>3</td>
<td>P3</td>
<td>0.0470</td>
</tr>
<tr>
<td>4</td>
<td>P4</td>
<td>0.0302</td>
</tr>
<tr>
<td>5</td>
<td>P5</td>
<td>0.0370</td>
</tr>
<tr>
<td>6</td>
<td>P6</td>
<td>ND</td>
</tr>
<tr>
<td>7</td>
<td>P7</td>
<td>ND</td>
</tr>
<tr>
<td>8</td>
<td>P8</td>
<td>0.0125</td>
</tr>
<tr>
<td>9</td>
<td>P9</td>
<td>ND</td>
</tr>
<tr>
<td>10</td>
<td>P10</td>
<td>ND</td>
</tr>
<tr>
<td>11</td>
<td>P11</td>
<td>ND</td>
</tr>
<tr>
<td>12</td>
<td>P12</td>
<td>ND</td>
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<tr>
<td>13</td>
<td>P13</td>
<td>ND</td>
</tr>
<tr>
<td>14</td>
<td>P14</td>
<td>1.345</td>
</tr>
<tr>
<td>15</td>
<td>P15</td>
<td>1.296</td>
</tr>
<tr>
<td>16</td>
<td>TP1</td>
<td>0.3367</td>
</tr>
<tr>
<td>17</td>
<td>TP2</td>
<td>0.647</td>
</tr>
<tr>
<td>18</td>
<td>TP3</td>
<td>1.392</td>
</tr>
</tbody>
</table>
The Cadmium contamination may occur in the soil in which these herbs are grown. Soils may be contaminated from industrial discharge, mine tailings, waste water irrigation, atmospheric depositions and/or waste disposal containing heavy metals (Krishna et al., 2009).

Table 2. Concentration range of cadmium (ppm) in all samples of herbal tooth care products.

<table>
<thead>
<tr>
<th>Concentration Range of Cadmium</th>
<th>Frequency</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0 – 0.3</td>
<td>13</td>
<td>72</td>
</tr>
<tr>
<td>0.4 – 0.7</td>
<td>2</td>
<td>11</td>
</tr>
<tr>
<td>1.3 – 1.4</td>
<td>3</td>
<td>17</td>
</tr>
</tbody>
</table>

The concentration range of Cd in all 18 samples is shown in Table 2. Most of the samples (13) had concentrations in the range 0.0 – 0.3 ppm, while only two samples had concentrations in ranging from 0.4 –0.7ppm. Three of the samples contained cadmium ranges of 1.3 – 1.4 ppm. This shows that majority of the herbal tooth powders are safe to use.

4. Discussion

Zinsaza, et al. (2015) conducted a similar study in Tehran, Iran which used a highly reactive and selective method to measure copper, lead and cadmium in seven herbal syrups available in herbal product stores of the city. In this study, the mean concentrations were calculated cadmium 66.926 μg/L, copper 5.95μg/L, and lead 6.269 μg/L. Thus, the concentrations were below the standard limits set by the WHO. In our study, most herbal powders had cadmium amounts below the WHO standard limits, only a few samples had elevated Cd levels, which could be high enough (1.34 ppm on average) to cause toxic effects to lungs and kidneys (WHO, 2010).

Another study conducted by Saeed, et al. (2010) dealt with the estimation of heavy metal concentrations in herbal drugs manufactured in Pakistan. Twenty-five herbal products manufactured by well-known companies were chosen. Results showed that heavy metals such as cadmium, lead, chromium and nickel exceeded the acceptable limits published by the International Regulatory Authorities. In comparison to this research, only five samples were showed similarities because cadmium concentrations in herbal tooth care products were very high as compared to the permissible limits established by the WHO. Because of the data from the 2010 studied showed high contamination levels, the authors passed this information to the Ministry of Health and suggested the establishment of rules and regulations for authentication of herbal products on scientific grounds. The goal would be to protect consumers from any adverse effects from heavy metals contamination in herbal products (Saeed et al., 2010).

Ekeanyanwu, et al. (2013) investigated concentrations of heavy metals (chromium, cadmium, nickel, copper and manganese) in herbal products gathered from local drug stores of well-known manufacturers in Nigeria. The researches also used AAS (Atomic Absorption Spectrophotometer). The concentration of cadmium in samples was in the low range of 0.002 – 0.003μg/g. These results are somehow similar to the results of the current study, but contrary in a way because most samples of this study had relatively higher Cd concentrations, those of which were still within the WHO standards. However, quite a few samples exceeded the standards. According to the doses recommended by manufacturers, the daily intake of cadmium was calculated to be 0.04 – 0.18. The tested products had low concentration of Cd because the daily intake was below the standard limit.

Hajra, et al. (2015) calculated heavy metals concentrations in herbal and Ayurvedic medicines from local markets in Hazara, Pakistan. The analysis included ten liquid preparations collected from shops in Mansehra and Abbottabad, Pakistan.

Karayil, et al. (2014) researched the concentrations of heavy metals in the plant extracts collected from the hill ranges of the Palakad District of Kerala, India. The results showed that the samples had the following leverls: cadmium (0.053 ppm), arsenic (0.60 ppm), manganese (0.017 ppm), chromium (0.036 ppm), copper (1.637 ppm), lead (0.002 ppm), zinc (0.247 ppm) and mercury (0.0 ppm).

Different regulatory bodies have established enough documentation to classify Cd as a human carcinogen. The most persuasive evidence comes from increasing cases of lung cancer in workers who are exposed to Cd by breathing. It also comes from studies conducted on animals which show that cadmium exposure can produce cancers in the in various organs (Waalkes, 2013). There is no evidence of the harmful effects of Cd on reproductive system caused by environmental and occupational exposure to cadmium (Nordberg et al., 2007).

Environmental pollution produced from human activities can cause higher heavy metal contamination in
plants used as herbal medicines. Some sources include discharges from industrial facilities, leaded petrol, agrochemicals, cadmium-containing composts, natural mercury, and pesticides with arsenic that are still in use in some countries.

Contamination of herbal products can occur at any production phase, from developing conditions to outside drying, manufacturing and preservation. However, sometimes metals are purposefully added to Asian herbal products because in the light of the fact that traditional Chinese and Indian herbal products are thought to have therapeutic effects.

5. Conclusion
This study showed that all herbal tooth powder samples have either detectable or non-detectable amounts of cadmium in varying concentrations. The concentrations of Cd in most of the samples under study were below the permissible limit approved by FAO/WHO (0.3 mg/Kg). The results obtained showed that few samples of herbal tooth powders have high concentrations of Cd and are likely to pose serious health risk to consumers. However, since tooth care products are used daily, higher levels of Cd could result and increase the risk of health problems. Because of possible health risk, there is a need to establish national permissible limits for different heavy metals in herbal products in Pakistan. Moreover, there must be effective enforcement measures so that companies manufacturing herbal products produce safe ones free of contaminants.

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References


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تحديد نسبة cadmium في مساحيق الأسنان العشبية المشترأة من السوق المحلية في لاہور

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الملخص

تم تصميم هذه الدراسة لتحديد نسبة تركيز cadmium (Cd) في مساحيق الأسنان العشبية التي يتم بيعها في الأسواق المحلية في لاہور باستخدام مقياس الامتصاص الديني الطيفي، وكذلك مقارنة تركيز cadmium مع الحد المسموح به من منظمة الصحة العالمية. تم تحديد تركيزات cadmium في 15 عينة من مساحيق الأسنان العشبية، مما تم تحليل تركيزه في ثلاثة أنواع من معاجين الأسنان العشبية وذلك لمقارنة تركيزه في تلك المعاجين مع تركيزه في مساحيق تنظيف الأسنان العشبية. تم إخضاع عينات من مساحيق تنظيف الأسنان العشبية لعملية الهمض الحمضي باستخدام HClO₄ و HNO₃ و H₂O، وتحليل محاولات العينة باستخدام الامتصاص الديني الطيفي (AAS). تم اكتشاف cadmium في 8 عينات ولم يتم اكتشافه في 7 عينات. أظهرت النتائج أنه تم تسجيل cadmium في نطاق بين 0 جزء في المليون و1.392 جزء في المليون في مساحيق عشبية مختلفة. كان متوسط تركيز cadmium في مساحيق الأسنان العشبية هو 0.30 جزء في المليون وكان في معاجين الأسنان العشبية 0.7919 جزء في المليون. كانت تركيزات cadmium في معظم العينات قيد الدراسة ضمن الحد المسموح به المعتاد من قبل منظمة الصحة العالمية (0.3 جزء في المليون). وأظهرت النتائج التي تم الحصول عليها أن معظم مساحيق الأسنان العشبية (67% البقاء) الموجودة في الأسواق المحلية المختلفة في لاہور لديها تركيزات منخفضة من cadmium ولا تشكل أي خطر على صحة الإنسان. من الضروري وضع حدود طبية مسموح بها لمختلف المعادن الختیلة للمساحيق العشبية في باكستان لتطوير إجراءات تنفيذ فعالة للامتثال للقوانين واللوائح البيئية.