QUANTITATIVE EVALUATION OF BIOACCUMULATING TOXIC AND ESSENTIAL METALS IN VEGETABLES PROCURED FROM LOCAL MARKETS OF PAKISTAN AND THEIR PUBLIC HEALTH RISK ASSESSMENT

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ABSTRACT

Heavy metals uptake were determined in eleven vegetables procured from local market of Karachi and Lahore while results were compared with permissible safe limits set by WHO, SEPA (China) and FSSA (India) to ascertain their public dietary exposure and health hazards. Important findings included: Average concentrations of Pb were exceeding permissible level of WHO and FSSA in onion procured from Karachi and in carrot, potato, bitter gourd and apple gourd from Lahore. Although Cd metal was more accumulated than safe limits set by SEPA in most of vegetable samples from Karachi however it was within permissible range in all vegetables from Lahore. Moreover, average quantity of Zn were exceeded than FSSA set values in onion, bell pepper, ridge gourd, bitter gourd and apple gourd from Karachi as well as in onion, bell pepper, cucumber, taro, carrot and apple gourd from Lahore whereas amount of Fe and Mn metals were found well within safe control of WHO standards in all vegetables from both cities. Daily Intake of Fe and Mn metals were yielded within safe range of reference oral dose values but exceeded in case of Pb, Cd and Zn metals. Calculated Health Risk Index values were found more than one (>1) for Pb, Cd and Zn metals while less than one (<1) for Fe and Mn metals.

Key words: Heavy metals, Vegetables and Health Risk Index.

INTRODUCTION

Vegetables are generally consumed with the main course of meal in both cooked and uncooked forms (Potter and Hotchkiss, 1995). Vegetables provide essential vitamins, fibers and minerals, which are vital for human health (Marbaniang et al., 2012). Based on their function, metals can be classified as toxic and essential metals (Belitz et al., 2009). Results of various research studies have shown that vegetables contain both toxic and essential metals over a wide range of concentrations (Radwan and Salama, 2006; Sharma et al., 2009; Othman, 2010; Sobukola et al., 2010; Marbaniang et al., 2012; Singh et al., 2012). Ingestion of contaminated vegetables is an important route of heavy metals migration into human body. Factors that influenced the uptake of these metals by plant roots and its subsequent translocation to the stem, leaves and vegetables/fruits are: plant genetics, metal concentration in the soil solution, ease of transport from root to shoot, and irrigation malpractices (Pehluvan et al., 2012; Khadeeja et al., 2013; Yasar et al., 2013; Aslam et al., 2015).

Pb and Cd metals are cytotoxic and capable to accumulate in various vegetables. Pb can cause damages to kidneys, cardiovascular tissues, immune, hematopoietic, central nervous and reproductive systems while Cd associated with bone demineralization, renal dysfunction, impair lung function and increase the risk of lung cancer (Graeme and Pollack, 1998). Fe is an essential metal and required about 60 mg/person/day for normal functioning of human body. Fe is mainly present in hemoglobin (blood) and myoglobin (muscle tissue) pigments (Belitz et al., 2009). Zn and Mn are also essential elements. However, high intake of Zn is toxic for human, on contrary Mn is relatively nontoxic even in higher amount. Daily intake requirements of human body are 10-40 mg of Mn and about 2-48 mg of Zn (Belitz et al., 2009).

MATERIALS AND METHODS

All the chemicals and reagents used in this study were of analytical grade and purchased from Merck (Darmstadt, Germany).

Sample Preparation: Eleven vegetables were selected and purchased from local markets of Karachi (campus shop of Karachi University and main vegetable market) and Lahore (Kot lakhpat vegetable market). These procured vegetables were identified by an agricultural scientist and included onion, bell pepper, cucumber, turnip, eggplant, taro, ridge gourd, carrot, potato, bitter gourd and apple gourd. All vegetables were washed properly with tap water and then rinsed with deionized water to remove dust and other contaminations. The vegetables were cut into small pieces and dried at 105 °C. Vegetables were ground with porcelain mortar and pestle.
Determination of Health Risk Index (HRI): The health risk index was calculated for Pb, Cd, Zn and Mn by using the following formula (Khan et al., 2010):

$$\text{HRI} = \frac{\text{DIM}}{\text{RfD}}$$

Where, \( \text{DIM} \) = Daily intake of metals and \( \text{RfD} \) = Reference (oral permissible) dose

If the value of HRI is less than 1 it means that the population consuming the vegetables is safe.

RESULTS AND DISCUSSION

In past decades, food safety became a public concern worldwide. Consequently, more and more research studies were conducted to evaluate the risks of consuming foodstuffs that were contaminated by pesticides, heavy metals and toxins (Radwan and Salama, 2006; Sharma et al., 2009; Othman, 2010; Sobukola et al., 2010; Singh et al., 2012). Some research studies in Pakistan reported the concentration of metals in vegetables. A study conducted by Mahmood et al. (2014) had compared the metals accumulation and health risk assessment of vegetables that were grown in Lahore using waste water and ground water. Results of this study had shown that soil and vegetables irrigated with waste water were enriched with various heavy metals which were harmful for health. Khan et al. (2010), Ismail et al. (2011) and Ahmed et al. (2012) had reported the concentration of heavy metals in vegetables that were grown in Gilgit, Hyderabad and Rawalpindi respectively. Abbas et al. (2010) had reported the concentration of Pb, As and Hg in various vegetables of Sindh. Whereas Parveen et al. (2003) and Khadeeja et al. (2013) had reported the concentration of trace metals in some vegetables of Karachi.

Toxic and Essential Metals in Vegetables: Demand of food crops has increased in developing countries due to rapid urbanization. Hence, waste water irrigation became a common trend (Singh et al., 2012). Karachi is one of the cities where farmers used waste water for irrigation due to shortage of fresh water (Yousufzai et al., 2001; Saif et al., 2005). In present study a survey was conducted to identify the major supply source of vegetables in different shops. It was found that most of the vegetables were delivered to the shops from Malir fields which have geographical positioning parameters of 24.9224029 latitude & 67.2509193 longitudes. As Malir fields are situated along bank of Malir drain therefore generally waste water is used to irrigate the food crops. Lahore is another city of Pakistan facing challenges of urbanization and industrialization where resultant anthropogenic activities had polluted fresh water resources (Mahmood and Malik, 2014). As this trend of polluted water irrigation is on rise therefore, it is important to start regular monitoring programs and surveys in order to study metal contents in vegetables.
This study is one step ahead towards this direction and results of this study presents the level of toxic (Pb & Cd) as well as essential metals (Fe, Zn & Mn) that were found in the vegetables that were purchased from the local markets of Karachi and Lahore cities (Table 1 & Fig. 1).

**Pb Profile:** Comparison of average concentrations of Pb in various vegetables procured from the local markets of Karachi and Lahore was exhibited in Fig. 1(a). Onion from Karachi and apple gourd from Lahore contained the highest level of Pb 7.484 ppm and 7.308 ppm respectively. On the other hand, lowest levels of Pb were detected in ridge gourd from Karachi and eggplant from Lahore which consist of 0.0014 ppm and 0.362 ppm of Pb respectively. Furthermore, three vegetables of Karachi (cucumber, bitter gourd and apple gourd) and six vegetables of Lahore (onion, bell pepper, cucumber, turnip, taro and ridge gourd) did not contain Pb. Results of present study revealed that 72.72 % vegetables from Karachi and 45.45 % vegetables from Lahore were contaminated with Pb. Average concentrations of Pb in vegetables procured from local market of Karachi were compared with the results of other studies in Table 2. It was found that the average concentration of Pb in eggplant, onion, and potato was higher than the values reported by Abbas et al. (2010), Ahmad et al. (2012) and Parveen et al. (2003). On contrary, the average concentration of Pb found in bell pepper was less as compared to the value reported by Ahmad et al. (2012). Table 2 also showed the comparison of average concentration of Pb in vegetables that were purchased from Lahore. The average concentration of Pb in eggplant, potato and bitter gourd was relatively higher than the values reported by Abbas et al. (2010) however, the average concentration of Pb in eggplant was lower than the values reported by Ahmad et al. (2012). On comparison with the permissible limits set by WHO (0.3 ppm) and FSSA (2.5 ppm) (Khan et al., 2010), it was found that average concentration of Pb was beyond the limit in onion from Karachi and four other vegetables from Lahore (carrot, potato, bitter gourd and apple gourd). However, the average concentrations of Pb in different vegetables procured from Karachi and Lahore were found within the SEPA permissible limits as SEPA standards have set permissible limits for Pb at higher value i.e. 9 ppm (Khan et al., 2010).

**Cd Profile:** Comparison of the average concentrations of Cd in vegetables procured from the local markets of Karachi and Lahore was exhibited in Fig. 1(b). Highest levels of Cd were observed in turnip (1.178 ppm) from Karachi and onion (0.162 ppm) from Lahore. On contrary, lowest levels of Cd were found in onion (0.266 ppm) from Karachi and bell pepper (0.122 ppm) from Lahore. Cd was not detected in four vegetables (bitter gourd, ridge gourd, cucumber and potato) of Karachi and eight vegetables (cucumber, turnip, taro, ridge gourd, potato, carrot, bitter gourd and apple gourd) of Lahore. Result of current study has ascertained that about 63.63 % vegetables from Karachi and 27.27 % from Lahore were contaminated with Cd. Average concentrations of Cd in vegetables procured from local market of Karachi were compared with the results of different studies in Table 2. It was found that the average concentration of Cd in eggplant, onion, and turnip from Karachi was higher than the values reported by Abbas et al. (2010) and Parveen et al. (2003). On contrary, the average concentration of Cd found in bell pepper was less as compared to the value reported by Ahmad et al. (2012). Upon comparison of results in vegetables from Lahore (Table 2) it was observed that average concentration of Cd in onion was relatively higher than the values reported by Abbas et al. (2010) and Parveen et al. (2003) however, the average concentrations of Cd in eggplant and bell pepper were lower than the values reported by Ahmad et al. (2012) and Parveen et al. (2003). Moreover, the average concentrations of Cd in vegetables from Karachi were higher than permissible limits (0.2 ppm) set by SEPA (Khan et al., 2010). On contrary the values were within the limits for the vegetables from Lahore. Furthermore, comparing results with the permissible limit set by FSSA have shown that the average concentrations of Cd were within safe range as FSSA standards have set permissible limit for Cd at higher value i.e. 1.5 ppm (Khan et al., 2010) (Table 1 & Fig. 1(b)).

**Fe Profile:** Highest levels of Fe were found in onion from Karachi (34 ppm) and in turnip from Lahore (84.4 ppm). On the other hand, the lowest levels were observed in eggplant from Karachi (1.28 ppm) and turnip from Lahore (9.3 ppm) (Table 1). Comparison of the average concentrations of Fe in vegetables procured from the local markets of Karachi and Lahore is exhibited in Fig. 1(c). According to the present study, the average concentration of Fe in most of the vegetables purchased from local market of Karachi was higher than the concentration reported by the other researchers (Parveen et al., 2003; Sharma et al., 2009; Abbas et al., 2010; Ismail et al., 2011; Ahmed et al., 2012). However, average concentration of Fe in cucumber purchased from local market of Lahore was 10 ppm which was lower than the value (13.6 ppm) reported by Ahmed et al. (2012) but higher than the study reported by Ismail et al. (2011). Average concentrations of Fe in different vegetables procured from Karachi and Lahore were found within the WHO permissible limits in subject study as WHO standards have set permissible limit for Fe at higher value i.e. 425 ppm (Codex, 2007).

**Zn Profile:** Highest levels of Zn were found in apple gourd from Karachi (116 ppm) and bell pepper from Lahore (164 ppm). While lowest levels were observed in potato from Karachi (6.5 ppm) and egg plant from Lahore (20 ppm) (Table 1). Comparison of average
concentrations of Zn in vegetables procured from the local markets of Karachi and Lahore has shown in Fig. 1(d). Comparison of these results with previous studies revealed that the average concentration of Zn in cucumber (40 ppm), eggplant (34 ppm) and onion (74 ppm) from Karachi was higher than the values reported by Ismail et al. (2011), Parveen et al. (2003), Radwan and Salama (2006). Similarly, the average concentration of Zn in bell pepper from Karachi was 68 ppm, which was higher than the value reported by Ahmed et al. (2012). While average concentration of Zn in apple gourd procured from Karachi and in bell pepper and cucumber procured from Lahore were exceeded these permissible limits. Comparison of the results with the permissible limits set by FSSA (50 ppm) (Khan et al., 2010) showed that the average concentrations of Zn in onion, bell pepper, ridge gourd, bitter gourd and apple gourd procured from Karachi were exceeded than permissible limits while in case of Lahore onion, bell pepper, cucumber, taro, carrot and apple gourd contained Zn concentrations higher than threshold standard set by FSSA (Table 1).

Mn Profile: Comparison of the average concentrations of Mn in vegetables procured from the local markets of Karachi and Lahore was displayed in Fig. 1(e). The highest levels of Mn were found in carrot from Karachi (5.4 ppm) and bitter gourd from Lahore (4.4 ppm). On contrary, lowest levels of Mn (0.4 ppm) were found in apple gourd from Karachi and bell pepper from Lahore. In addition, Mn was not detected in eight vegetables from Karachi (eggplant, ridge gourd, potato, cucumber, onion, bitter gourd, turnip and taro) and seven vegetables from Lahore (ridge gourd, potato, carrot, onion, apple gourd, turnip and taro).

According to present study, the average concentration of Mn in carrot of Karachi was found 5.4 ppm which was higher than the value (1.2 ppm) reported by Ismail et al. (2011). On the other hand the value in bell pepper (1.00 ppm) from Karachi was lower than the value (8.8 ppm) reported by Ahmed et al. (2012). Among the vegetables from Lahore, the average concentration of Mn in cucumber (0.6 ppm), bell pepper (0.4 ppm) and eggplant (3.8 ppm) was found lower than the values reported by Ahmed et al. (2012). Furthermore, concentration of Mn in cucumber was also measured less than the value reported by Ismail et al. (2011). In addition, concentration of Mn in bitter gourd and eggplant was higher than the values reported by Ismail et al. (2011).

Comparison of the results showed that the average concentrations of Mn in different vegetables procured from Karachi and Lahore were found within the WHO permissible limits as WHO standards have set permissible limit for Mn at higher value i.e. 500 ppm (Table 1; Codex, 2007).

Daily Intake of Metals (DIM): Computed values of daily intake of metals (DIM) due to the consumption of vegetables procured from local market of Karachi were shown in Fig. 2. Reference oral dose values for Pb, Cd, Zn and Mn were 4×10⁻³, 1×10⁻³, 3×10⁻¹ and 3.3×10⁻² mg/person/day respectively (Mahmood and Malik, 2014). The Reference oral dose for Fe was 60 mg/person/day (Jolly et al., 2013). Comparison of the DIM values with reference oral dose had indicated that the values were within the limit for Fe and Mn. However the DIM values of Pb calculated for onion, turnip, eggplant, taro and ridge gourd had surpassed the reference oral dose value. The DIM values of Cd calculated for all the vegetables procured from Karachi were exceeded than reference oral dose value while only DIM values of Zn calculated for onion, bell pepper, ridge gourd and apple gourd were yielded above the reference oral dose value.

Calculated values for daily intake of metals (DIM) due to the consumption of vegetables procured from local market of Lahore were plotted in Fig. 2. Comparison of the DIM values with reference oral dose values indicated that the values were within the limit for Cd, Fe and Mn. However the DIM values of Pb calculated for carrot, potato, bitter gourd and apple gourd were exceeded from reference oral dose value while in case of Zn it had gone beyond the reference oral dose value for onion, bell pepper, cucumber, taro and carrot. DIM values of this study were compared with results of Khan et al. (2010) and were found to be consistent for Pb where the calculated DIM value elevated above reference oral dose value. However the DIM results of Cd obtained for the vegetables procured from Karachi, were not in agreement with results reported by Khan et al. (2010) where the calculated DIM was within the reference oral dose value.

Health Risk Index (HRI): Health risk index greater than one, indicates that the consumption of such vegetables can provoke health risk to the people using these vegetables in their daily diet. Computed HRI values for metals due to the consumption of vegetables procured from local market of Karachi have been exhibited in Fig. 2. It was found that the HRI of Pb obtained for onion, turnip, eggplant, taro and ridge gourd was more than one. HRI of Cd obtained for all the vegetables procured from Karachi was greater than one. HRI of Zn obtained for
Table 1. Permissible limits of heavy metal and their concentrations in various vegetables of Karachi and Lahore.

<table>
<thead>
<tr>
<th>International Standards</th>
<th>Pb</th>
<th>Cd</th>
<th>Fe</th>
<th>Zn</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEPA China permissible limits</td>
<td>9</td>
<td>0.2</td>
<td>-</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>FSSA India permissible limits</td>
<td>2.5</td>
<td>1.5</td>
<td>-</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>WHO permissible limits</td>
<td>0.3</td>
<td>0.1</td>
<td>425</td>
<td>100</td>
<td>500</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Plant Species</th>
<th>Vegetable</th>
<th>Concentration of heavy metals in vegetables (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Allium cepa</em> L.</td>
<td>Onion</td>
<td>KHI: 7.484, LHR: 0.266</td>
</tr>
<tr>
<td><em>Capsicum annuum</em></td>
<td>Bell pepper</td>
<td>KHI: 0.002, LHR: 0.45</td>
</tr>
<tr>
<td><em>Cucumis sativus</em> L.</td>
<td>Cucumber</td>
<td>KHI: 0, LHR: 6</td>
</tr>
<tr>
<td><em>Brassica rapa</em> L.</td>
<td>Turnip</td>
<td>KHI: 1.54, LHR: 25</td>
</tr>
<tr>
<td><em>Solanum melongen</em> L.</td>
<td>Egg plant</td>
<td>KHI: 1.97, LHR: 3.2</td>
</tr>
<tr>
<td><em>Colocasia esculenta</em> L.</td>
<td>Taro</td>
<td>KHI: 1.416, LHR: 31.2</td>
</tr>
<tr>
<td><em>Luffa acutangula</em> L.</td>
<td>Ridge gourd</td>
<td>KHI: 0.0014, LHR: 31.2</td>
</tr>
<tr>
<td><em>Daucus carota</em> L.</td>
<td>Carrot</td>
<td>KHI: 0.334, LHR: 31.2</td>
</tr>
<tr>
<td><em>Solanum tuberosum</em> L.</td>
<td>Potato</td>
<td>KHI: 0.816, LHR: 31.2</td>
</tr>
<tr>
<td><em>Momordica charantia</em> L.</td>
<td>Bitter gourd</td>
<td>KHI: 0, LHR: 31.2</td>
</tr>
<tr>
<td><em>Praecitrullus fistulosus</em></td>
<td>Apple gourd</td>
<td>KHI: 0, LHR: 31.2</td>
</tr>
</tbody>
</table>

Table 2. Comparison of the average concentration of Pb and Cd found in various vegetables of Karachi and Lahore with the results of other previous studies.

<table>
<thead>
<tr>
<th>Study Reference</th>
<th>Bitter gourd</th>
<th>Potato</th>
<th>Onion</th>
<th>Cucumber</th>
<th>Egg plant</th>
<th>Bell pepper</th>
<th>Turnip</th>
<th>Carrot</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present Study (KHI)</td>
<td>NT 0.816 NT 7.484 0.266 NT 1.97 0.368 0.002 0.45 1.54 1.178 0.334 1.046</td>
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<tr>
<td>Present Study (LHR)</td>
<td>NT 6.266 NT 0.162 NT 0.362 0.136 NT 1.14 0.1 1.64 0.85</td>
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<tr>
<td>Mahmood et al. (2014)</td>
<td>ND 0.21 ND 0.21 ND ND ND ND ND ND 0.36 0.36 0.29 0.29</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Khadeeja et al. (2013)</td>
<td>ND ND ND ND ND ND ND ND ND</td>
<td></td>
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</tr>
<tr>
<td>Ahmed et al. (2012)</td>
<td>ND ND ND ND ND ND ND ND ND</td>
<td></td>
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<tr>
<td>Abbas et al. (2010)</td>
<td>0.018 0.016 0.091 0.04 0.006 0.079 0.069 0.037 0.036 0.025 ND ND ND ND ND ND ND ND ND ND</td>
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</tr>
<tr>
<td>Parveen et al. (2003)</td>
<td>1.52 0.31 0.16 0.08 0.06 0.07 1.72 0.36 1.3 0.31 ND ND ND ND ND ND ND ND</td>
<td></td>
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</table>

NT: not detected, ND: Not determined
onion, bell pepper, ridge gourd and apple gourd was more than one while it was less than one for Fe and Mn from all tested vegetables.

HRI values for metals due to the ingestion of vegetables procured from local market of Lahore have also been displayed in Fig. 2. It was found that the HRI of Pb obtained for carrot, potato, bitter gourd and apple gourd was more than one. HRI of Cd, Fe and Mn obtained for all the vegetables procured from Lahore was less than one while it was more than one for Zn from onion, bell pepper, cucumber, taro and carrot of Lahore.

Health risk assessment studies have been reported by some researchers who had identified high levels of Pb in the blood of children in Karachi (Rahbar et al., 2002) and high levels of Cd in school children of Lahore (Sughis et al., 2011). HRI results of this study were compared with studies of Khan et al. (2010) and Singh et al. (2012) and were found to be consistent for Pb (HRI > 1). The HRI results of Cd and Zn obtained in this study were compared with the results reported by Jolly et al. (2013) and were found consistent where the values of health risk index also raised above one for some vegetables.

Fig. 1. Comparison of heavy metal concentrations in various vegetables of Karachi and Lahore along with international permissible limits.
Fig. 2. Comparison of Daily Intake of Metals and Health Risk Index of various vegetables of Karachi and Lahore along with reference oral permissible dose limits.

**Conclusion:** On the basis of above mentioned results it was concluded that significant amount of Pb and Cd toxic metals have been build up in different vegetables auctioned in Karachi and Lahore markets probably due to large scale anthropogenic activities in these mega cities whereas some essential metals were also more accumulated in these vegetables. Generally, the extent of heavy metal enrichment in terms of ppm was found in the order of Zn > Fe > Pb > Mn > Cd. Research revealed that most of underground vegetables (root/tuber/bulbs etc) have a higher tendency to accumulate heavy metals as compared with the others aerial vegetables (leafy, stem, flower, buds etc) which indicated that main route of heavy metal bioaccumulation in plants was contaminated soil irrigated with polluted water. HRI indicated that the most of aerial vegetables sold in Karachi and Lahore markets were generally free from health risk; however, some underground vegetables pose a serious health risk, particularly in terms of Cd and Pb.

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