Available free online at www.medjchem.com

Mediterranean Journal of Chemistry **2018**, 6(6), 223-230

Evaluation of Toxic and Essential Metals in Some Selected Chewing Food Products and their Daily Intake by the Population of Karachi, Pakistan

Shahid Bhutto [1], Nusrat Jalbani [1,*], Akhtar Shareef [1], Mohammad Tahir [1], Razia Begum[1], Farooq Ahmed [1] and Suhail Ahmed [2]

[1] Center for Environmental Studies, Pakistan Council for Scientific and Industrial Research, Laboratories Complex, Karachi, Pakistan

[2] Center for Environmental Sciences, University of Sindh, Jamshoro, Pakistan

Abstract: The present study focused on different brands of chewing food products which containing some toxic metals (TMs) and essential metals and these samples were analyzed to determine the levels of some toxic metals (Pb, Cd, Ni, Cr and Mn) and essential metals (Ca, Cu, Fe, K, Mg, Na and Zn). The samples of gutka (100), sweet supari (63), sweet paan (16) and paan masala (21) were randomly collected from different shops of Karachi, Pakistan. The validity of conventional wet acid digestion method (CAD) was assessed by analyzing two certified reference materials (CRM) Virgina tobacco leaf (CTA-VTL-2) and Bovine liver (1577b) and standard addition recovery test. The limit of detections (LODs, n=10) of the method were found to be 0.144, 14.4, 8.89, 2.76, 4.06, 15.3 and 2.99, 22.9, 9.97, 4.54, 1.89, 1.76 µg L^{-1} for Ca, Cu, Fe, K, Mg, Na, Zn, Cd, Cr, Mn, Ni and Pb, respectively. The CAD method was successfully applied to real samples for the determination of toxic and essential metals.

Keywords: Chewing food products; toxic and essential metals; conventional wet acid digestion method; Atomic Absorption Spectrometry.

Introduction

The chewing food products (gutka, sweet paan, sweet supari (beetal nuts) and paan masala) are widely consumed products in Pakistan and as well as in many other Asian countries and elsewhere all over the world [1], although their regular intake has been interrelated with human health problems [2]. The formulation of the chewing products is similar to an addiction and used by all age groups but frequently used by adults because of cheapness, bright pouches, easy availability, sweet taste and vigorous misleading advertisements [3,4]. However, these chewable, as well as other consumer products, have a lot of harm but most of the peoples are unaware of the harmful and lethal affects [5]. Furthermore, the products may contain TMs which are of great concern and can directly affect on human health [6]. Elements such as Fe, Cu, Mn, and Zn are essential nutrients and they play an important role in biological systems [7,8]. Besides providing the sweet taste and aroma to peoples, the selected products can also constitute a serious hazardous effect depending on the relative levels [9]. These TMs may cause several chronic toxicities including impaired organ function, poor reproductive capacity, hypertension, tumors, damage the IQ level and hepatic dysfunction[10].

Several sample preparation techniques have been reported (Hana R *et al 2017* and Abimannan Arulkumar *et al 2017*) for pre-concentration and determination of essential and toxic metal in food samples [11,12].

Although the CAD method requires concentrated acid and high temperature for the decomposition of organic matter in the digestion of real samples [13]. Determination of toxic and essential metals in food samples by electrothermal/flame atomic absorption spectrometry (ETAAS/FAAS) has several advantages including good selectivity, speed, and fairly low operational cost. Direct determination of trace elements at extremely low concentration is often very difficult due to the insufficient sensitivity of the methods and the matrix interferences [14,15].

A literature survey (Tasneem GulKazi *et al 2010*) was conducted and indicated that there is a

**Corresponding author: Nusrat Jalbani*
Email address: nusratjalbani_21@yahoo.com
DOI: http://dx.doi.org/10.13171/mjc66/01711160925-bhutto

Received July 27, 2017
Accepted, August 13, 2017
Published December 16, 2017

very limited finding on the concentrations of metals in chewing products of different brands of Pakistan [16].

Therefore, the present study was aimed to highlight the misleading and hostile marketing adopted by different manufacturer companies, and also evaluate concentrations of essential (Ca, Cu, Fe, K, Mg, Na and Zn) and potentially toxic (Pb, Cd, Ni, Cr and Mn) metals in all chewable different brands of chewing food products (gutka, sweet paan, sweet supari (beetal nuts), paan masala) determined by ETAAS/FAAS. The chewing samples were collected from different shops of Karachi City, Pakistan. These samples were manufactured in the local market of Karachi, Pakistan but not imported by any other country. A total of 200 chewable food samples were purchased on a random basis. In the view of obtained results, this study showed the elemental contamination in chewing food products. It is hoped that these findings will be important for public health and as well for scientific needs.

Material and Methods

Reagents and glasswares

Analytical grades of nitric acid (65%) and reagents (E. Merck Darmstadt, Germany) were used. Ultra-pure water (UPW) was used throughout the experimental work. A stock standard solution (1000 mg L^{-1}) of essential and toxic metals was used and obtained from Merck, (Darmstadt, Germany). Furthermore, working standards of corresponding metals were prepared from the dilution of the stock standard solution on daily basis. For the validation of the proposed method, certified reference materials (CRMs) i.e. Virginia tobacco leaf (CTA-VTL-2) and bovine liver (1577b) were used.

Instrumentation

A Hitachi Model 5000 Z Flame Atomic Absorption Spectrometry was used for determination of Ca, Cu, Fe, K, Mg, Na, Mn and Zn in all understudy samples, and ETAAS was used for Cd, Ni and Pb determination following the instrument conditions and temperature programs of graphite furnace as mentioned in Table 1. The calibration curves for Cd (0.5-2.0 µg L^{-1}), Pb (10-30 µg L^{-1}), Cr (0.4-1.2 mg L^{-1}), Fe, Cu, Mn and Zn (0.4-2.0 mg L^{-1}), Ca, K, Na and Mg (0.5-1.5 mg L^{-1}) were established by using of working standard solutions. Hollow cathode lamps were used and operated at recommended current.

Table 1. Measurement Conditions for electrothermal Atomization Atomic Absorption Spectrometry.

Operating Parameters	**Cd**	**Cr**	**Pb**	**Ni**
Lamp current (mA)	7.5	7.5	7.5	**10**
Wavelength	228.8	359.3	283.3	**232**
Slit width (nm)	1.3	1.3	1.3	**0.2**
Cuvette	**Tube**			

Temperature Programming

Drying	80	120	30 Sec	80	120	**30 Sec**
Ashing	300	300	30	400	400	**30**
Atomization	1500	1500	10	200	200	**10**
Cleaning	1800	1800	3.0	2400	2400	**3.0**

Common Parameters

Sample volume	**10µL analyte**
Background Correction	**D^2 Lamp**
Carrier gas Argon	**200 mL/mint**

Sampling

In the present study, various chewing products such as gutka, sweet paan, sweet supari (beetal nuts) and paan masala samples were collected from the open market of Karachi, Pakistan. The samples were collected on random basis in the year of 2010-2011. Before analysis, all collected samples were homogenized in a food blender (Hongdun HWT).

Analysis of real samples

(0.5-1.0) g of wet samples in triplicate of gutka, sweet paan, sweet supari (beetal nuts) and paan masala were weighed in 100 mL of the conical flask and added 10 mL of HNO_3 to this mixture and then left the sample solution for overnight. After acid addition, samples were heated on an electric hot plate for 2 h at 250 ˚C until a complete colorless solution occurred. After cooling and adding the appropriate quantity of UPW, the resulting solutions were then filtered through a Whatman 42 filter paper into a 50 mL volumetric flask and were diluted with UPW up to the mark. Afterwards, the subsequent determination of under studied metals was performed by ETAAS/FAAS spectrometry. Blank samples were also treated in same way as samples were treated. The proposed procedure was applied to CRMs and real samples. Food samples were digested with the acid mixtures and can create major problems for some ETAAS/FAAS systems because of deposits on the interface cones and on the ion optics caused by high concentrations of dissolved solids. For this reason, long-term stability can be poor.

Results and Discussion

The chewing food products are usually consumed by all age group due to good taste and flavor but these products having the lack of nutritional value. Ingredients of chewing food products contain toxic materials such as tobacco that is present in them during manufacturing. Some manmade toxins are also added to chewing food products such as antibiotics, flavors, preservatives and colorants that can unintentionally contaminate food and also packaging materials used to keep food safe and fresh. Unintentional contamination may occur through environmental pollution of the water, air and/or soil [17,18]. Acute or chronic exposure to TMs can lead to damage nerve cells and have harmful effects on vital organs. Food safety laboratories performing these analyses are often high-throughput facilities and required a detection tool that is efficient and cost-effective. Cd, Cr, Mn, and Ni, levels in gutka sample were found significantly elevated and on the other hand, Pb level in sweet supari (Beetal Nut) was found highest (Table 2). The obtained results showed that the level of TMs i.e. Cd, Cr and Pb were found lowest in Paan masala. The Ni and Mn concentrations 0.455±0.02 $\mu g/g^{-1}$ and 17.6±0.23 $\mu g/g^{-1}$ respectively were lowest in sweet supari (beetal nut) samples as compare to Gutka, Sweet Paan and Paan Masala as noted in Table 2. It is clear from the results that most of the understudy samples were severely contaminated with understudy TMs.

Table 2. Determined concentration of Cd, Cr, Mn, Ni and Pb in Gutka, Sweet Supari (Betal nuts) and Paan Masala in $\mu g\ kg^{-1}$.

	Cd	Cr	Mn	Ni	Pb
Gutka	1.25±0.06	40.1±2.5	395±27	14.8±0.95	3.83±0.25
Sweet Paan	0.074±0.003	0.517±0.02	19±0.001	0.561±0.025	0.692±0.03
Sweet Supari	0.064±0.004	0.475±0.02	17.6±0.23	0.455±0.02	207±12
Paan Masala	0.054±0.003	0.163±0.01	26.5±1.2	0.685±0.03	0.587±0.02

At 95% confidence limit (n = 3),

Similarly, some essential elements (Ca, Cu and Fe) were also found a high level in gutka and K, Mg Na and Zn were high in Paan Masala (Table 3). On the contrary Ca, Cu, Mg Na and Zn were lowest in sweet paan (Table 3). Several studies have been published on mineral status in the diet, such as Ca, Zn and Fe would affect the potential risk of TMs [19-22].

Table 3. Determined concentration of Ca, Cu, Fe, K, Mg, Na, and Zn in Gutka, Sweet Paan, Sweet Supari (Betal nuts) and Paan Masala.

Sample	*Ca	**Cu	**Fe	*K	*Mg	*Na	**Zn
Gutka	104±5.8	95±12	953±29	5.31±0.15	2167±137	19.2±1.1	15.18±0.75
Sweet Paan	2.18±0.08	3.97±0.31	25.6±1.5	7.34±0.35	15.3±1.1	9.3±0.47	6.54±0.55
Sweet Supari	3.15±0.05	5.29±0.12	13.5±0.5	8.56±0.55	17.6±1.2	11.7±0.45	8.56±0.55
Paan Masala	2.28±0.08	4.21±0.21	68.3±2.1	18.2±0.98	2416±185	22.1±1.1	18.2±0.98
Average	27.9	27.1	265.1	9.9	1153.9	15.6	12.12

*$\mu g\ g^{-1}$, **$ug\ Kg^{-1}$, at 95% confidence limit,

Our data clearly showed that results of Ca, Cu, and Fe in chewing products differ significantly between Gutka and Other understudy chewable products (Table 3); The daily intakes calculated as 10gram consumption per day for all metal and compared with WHO/FDA Tolerable Daily Intake (TDI) in Table 7. All the values in Table 7 are below respective TDIs, however, the TDIs are for foods that are consumed after chewing for 30 to 60 seconds normally. On another hand, the understudy chewable products spat after a considerable time of chewing ranging between 20 to 60 minutes. This long duration is the significant factor because some of our understudies' TMs (Cd, Cr, and Ni) are group 1 carcinogenic according to International Agency for Research (IARC) and National Toxicology Program (NTP). However, one of the major ingredients of chewable products i.e. smokeless tobacco is also group one carcinogen according to IARC and NTP. Therefore, the actual risk to local population posed by TMs contamination remains to be examined. The Iron and Manganese levels in gutka samples were significantly higher among all understudy samples as can be seen in Fig. 1. Similarly, Magnesium concentration was maximum in Gutka and Paan Masala (Fig.2). The mean concentrations of these minerals inherently present in the chewing products are indicated as: Ca: 27.9 mg kg^{-1}, Cu: 27.1 µg kg^{-1}, Fe: 265.1 µg kg^{-1}, K:9.9 mg kg^{-1} Mg: 1153.9 mg kg^{-1}, Na: 15.6 mg kg^{-1}, and Zn: 12.12 µg kg^{-1} as shown in Table 3. The increase in the uptake of minerals and TMs in the human body is not easily digestible. Toxic metals were found in chewing products under the TDIs and that are mostly well recognized as environmental contaminants, which can probably be affected during the sample preparation procedure (Table 7).

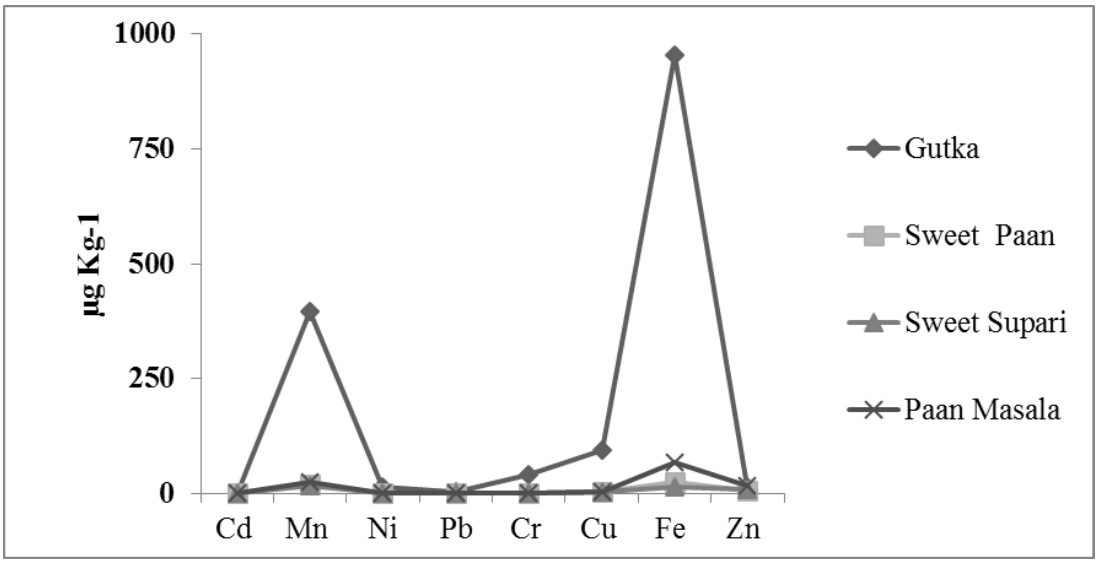

Figure 1. Mean level of selected hazardous and non-hazardous metals in the chewing products of Pakistan.

This is the first ever detailed study was carried out in Pakistan and it is very difficult to make inter-country comparisons. National authorities have the responsibility and obligation to ensure that chewing products such as gutka, sweet paan, sweet supari (beetal nuts) and paan masala are free from any environmental contamination and also free from naturally occurring toxins which may cause several human health problems.

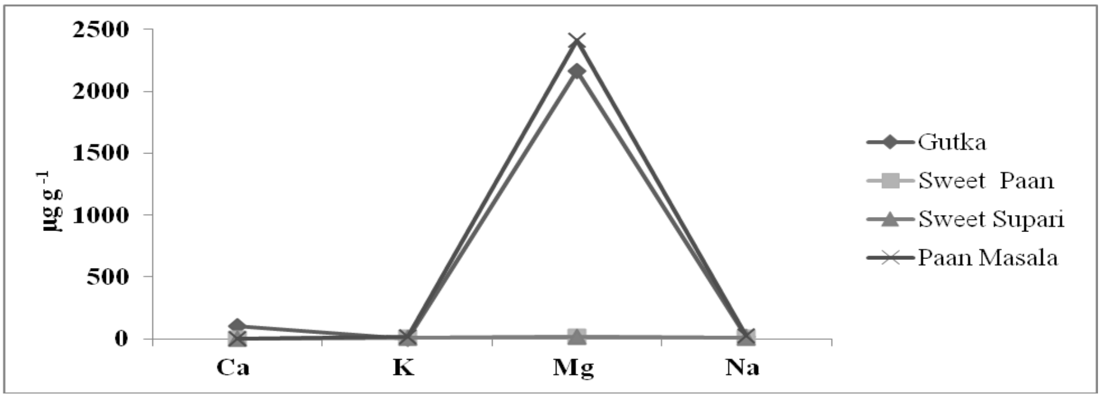

Figure 2. Mean level of selected non-hazardous metals in the chewing products of Pakistan.

Analytical figure of merit

Under optimized condition, the analytical figures of the proposed procedure were evaluated for the determination of Ca, Cu, Fe, K, Mg, Na, Zn, Cd, Cr, Mn, Ni and Pb in gutka, sweet paan, sweet supari (beetal nuts), paan masala samples. The calibration graph was established using standard solutions of all studied metals in analyzed samples. Linear range of the calibration curve for Cd (0.5-2.0 µg L^{-1}), Pb (10-30 µg L^{-1}), Cr, Ni (0.4-1.2 µg L^{-1}), Fe, Cu, Mn and Zn (0.4-2.0 mg L^{-1}), Ca, K, Na and Mg (0.5-1.5 mg L^{-1}) with the correlation coefficient (R^2) Ca: 0.9974, Cu: 0.9982, Fe: 0.9978, K: 0.9985, Mg: 0.9976, Na: 0.9983, Zn: 0.9997, Cr: 0.9982, Ni: 0.9984, Cd: 0.9985, Pb: 0.9979 and Mn: 0.9986. In order to confirm the applicability of the proposed procedure, the limit of detection (LOD) is defined as 3s, where s is the standard deviation of ten measurements of blank readings, LODs were found to be 0.1890, 0.0600, 0.0263, 0.0168, 0.0103, 0.0416, 0.0416, 0.0732, 0.0321, 0.0096, 0.0014, and 0.0014 mg L^{-1} for Ca, Cu, Fe, K, Mg, Na, Zn, Cd, Cr, Mn, Ni and Pb, respectively. The limit of quantification (LOQ), based on ten times the standard deviation of 10 measurements of a reagent blank and m as the slope of the calibration graph were 0.6320, 0.2001, 0.0875, 0.0560, 0.0337, 0.1387, 0.1389, 0.2440, 0.1070, 0.0321, 0.0047 and 0.0047 mg L^{-1} for Ca, Cu, Fe, K, Mg, Na, Zn, Cd, Cr, Mn, Ni and Pb, respectively.

$$LOD = 3 \times s / m \quad \text{and} \quad LOQ = 10 \times s / m$$

Table 4. Validation of the conventional wet acid digestion method (CAD) against certified reference material Virginia tobacco leaf (CTA-VTL-2) (µg g^{-1}, n=6) and Bovine Liver (1577b).

Toxic elements	Certified	CAD	%Recovery
	ẋ ± s	ẋ ± s	
Virginia tobacco leaf (CTA-VTL-2)			
Fe	184	183±11.5	99.5
Cd	0.5	0.505±0.032	101
Cu	160	159±9.6	99.4
Mn	10.5	10.3±0.47	98.1
Pb	0.129	0.128±0.009	99.2
Zn	127	128±8.2	101
Bovine Liver (1577b)			
Cr	1.87±0.16	1.84±0.063	98.4
Na	312	314±15.7	101
Ni	1.98±0.21	1.97±0.055	99.5
Mg	0.510±0.023	0.504±0.032	98.8
K	1.03±0.04	1.05±1.05	102

ẋ = mean, s = standard deviation (uncertainty)
at 95% confidence limit, x = mean value
%Recovery = (CAD Value / Certified Value) x 100

Validation of Methodology

In order to optimization, the conventional wet acid digestion method (CAD) procedure was applied to determine the Ca, Cu, Fe, K, Mg, Na, Zn, Cd, Cr, Mn, Ni and Pb from gutka, sweet paan, sweet supari (beetal nuts), paan masala and CRM samples. The accuracy of the proposed method was checked by the analysis of (Virginia tobacco leaf (CTA-VTL-2), bovine liver (1577b) CRM samples. Quantitative results for six replicate of CRMs recovery test showed a good agreement with the certified values, at 95% confidence limit, the results are given in Table 4. Similarly, other standard addition/recovery tests were performed on Gutka and Paan Masala samples to validate the CAD method at 95% confidence limit (Table 5 & 6).

Table 5. Standard Addition/recovery test in Gutka samples for determination of Cd, Cr, Mn, Ni and Pb (in ug Kg^{-1}).

Added Values	**Found Values**	**% Recovery**
Cadmium (Cd)		
0.0	1.25±0.06	**…..**
1.0	2.245	**99.5**
Chromium (Cr)		
0.0	40.1±2.5	**……**
5.0	44.95±2.7	**97.0**
Manganese (Mn)		
0.0	395±27	**…..**
5.0	399.8±12.5	**96.0**
Nickel (Ni)		
0.0	14.8±0.95	**…..**
10	24.5±1.4	**97.0**
Lead (Pb)		
0.0	3.83±0.25	**….**
10	**13.8±0.79**	**99.7**

*ug Kg^{-1} at 95% confidence limit,
%Recovery = (Standard Recovered / Standard added) x 100

Table 6. Standard Addition recovery test in Paan Masala samples for determination of Cd, Cr, Mn, Ni and Pb (μg Kg^{-1}).

Added Values	Found Values	% Recovery
	Cadmium (Cd)	
0.0	2.28±0.08	**…..**
1.5	3.76±0.23	**98.7**
	Copper (Cu)	
0.0	4.21±0.21	
1.0	5.21±0.34	**100**
	Iron (Fe)	
0.0	68.3±2.1	
5.0	73.1±2.6	**96.0**
	Potassium (K)	
0.0	18.2±0.98	
4.0	22.1±1.1	**97.5**
	Magnesium (Mg)	
0.0	2415±185	
5.0	2419.9±55.8	**98.0**
	Sodium (Na)	
0.0	22.1±1.1	
10	31.8±1.4	**97.0**
	Zinc (Zn)	
0.0	18.20±0.98	**…..**
1.5	**19.65±0.99**	**96.7**

at 95% confidence limit,
%Recovery = (Standard Recovered / Standard added) x 100

Essential and toxic metals in chewing food products and their daily intake Toxic metals are released into water, plants, soil, and food by natural and human activities [23-27]. Due to that reason, it is important to determine the concentrations of TMs in different chewing food samples. Abnormal ingestion causes neurological anomalies, hepatic and renal disturbances [28]. The proposed method was selected to cover a wide range of essential and toxic metals contents. The selected foods were gutka, sweet paan, sweet supari (beetal nuts) and paan masala are the most popular chewable food items which are being used by Karachi peoples because of its low cost and these food items are consumed by all age group but especially consumed by a male. The regular consumption of studied varieties may develop hypertension which may lead to heart or brain stroke and many other diseases including mouth cancer, though they are controllable, sometimes creates a lot of harm to health.

This trace and TMs were found within maximum TDIs limit in food in understudy samples and have adverse impacts on human health. The essential metals (Ca, Cu, Fe, K, Mg, Na, Zn, and Mn) become toxic and cause serious health issues, if taken in high quantities. Similarly, TMs might get deposited in the human body (especially in mouth) and caused long-term ill-effects on health. The TMs can directly or indirectly damage the DNA, which increases the risk of cancer. Human exposure to TMs can be different greatly due to use of different type of foods and manufacturing processes and occupational sources of TMs [29-31].

The present study illustrated that the intake of essential and toxic metals is different in different types of chewable food items in Karachi, Pakistan and provides specific information on the average dietary intake of studied metals as given in Table 7.

Moreover, the present study showed that toxic metals were detected in all products but these metals were founded at a low level in most of the chewable food items gutka, sweet paan, sweet supari (beetal nuts) and paan masala as compared to TDIs permitted levels (Table 7). These heavy metals are most responsible for major and minor contribution to cause serious health issues, as these metals are considered as a toxic even in ultra-small doses. The average consumption of these chewable food items was estimated by this survey on the population of different areas of Karachi city, Pakistan. The daily intakes of studied metals were calculated on the consumption of a minimum five pack 10gm (1 pack=2.0 gm)/person/day of the chewable food items and compared with permitted levels which recommended by WHO/FDA [32,33].

Table 7. Daily intake of Essential and toxic metals by consumption of some selected chewing food products (mg of metals based on 10gm gutka, sweet paan, sweet supari, and paan masala/person/day).

Metals	Gutka	Sweet Paan	Sweet Supari	Paan Masala	Tolerable Daily
	(mg or ug) of metals/day/person				mg or
Pb*	0.038	0.007	2.07	0.006	200
Cd*	0.012	0.0007	0.0006	0.0005	3
Ni*	0.148	0.006	0.004	0.007	300-600
Cr*	0.401	0.005	0.005	0.002	120
Mn*	3.95	0.17	0.176	0.26	2000-3000
Ca	1.04	0.031	0.031	0.023	1000
Cu*	0.95	0.053	0.053	0.042	10000
Fe*	9.53	0.25	0.135	0.68	8000-18000
K	0.053	0.086	0.085	0.18	1600
Mg	21.67	0.17	0.176	24.2	350-400
Na	0.192	0.12	0.117	0.22	2300
Zn*	0.152	0.08	0.085	0.18	12000-15000

* ug (including intake limits)
WHO/FAO Reference Daily Intakes reported above are for adults only.

Conclusion

The CAD method was used for determination of toxic and essential metals in different chewing food products which were collected from the supermarket of Karachi, Pakistan. In Gutka and Sweet Supari samples, TMs such as Cd and Pb concentrations were found higher as compare to other understudy chewing products. Mostly, the studied chewing food items are taken by low-income people and they are using on daily basis. Despite the fact that, an excess ingestion of these chewing products not only has an impact on human health but also affect the environment. Regarding the polluted environment, humans are exposed the TMs by ingestion of food which may lead to serious health risks. According to our findings, all studied samples holds up to 70 % market of tobacco products in Pakistan; its consumption is very high so the most of the peoples are suffering from many incurable diseases. For better check and balance of food products, concerned authorities should control and explore healthy products for the local population. Further, it is also recommended for another researcher to evaluate the extraction and retention of TMs in the mouth and to study the correlation of mouth cancer to these TMs.

References

1- S. Han, W. Yi, Yong-Yong Xu. *Asia Pac. J. Public Health*. **2013**.

2- T. M. Mack, *The Lancet*, **2001**, 357 (9269):1638–9.doi:10.1016/S0140 6736(00)04860-1.

3- M. Senn, F. Baiwog, J. Winmai, I. Mueller, S. Rogerson, N. Senn, *Drug and Alcohol Dependence*, **2009,** 105 (1-2), 126-131.

4- M. Ghaedi, A. Shokrollahi, A.H. Kianfar, A.S. Mirsadeghi, A. Pourfarokhi, M. Soylak, *J. Hazard. Mater*. **2008**, 154, 128–134.

5- F.E. Khansari, M. Ghazi-Khansari, M. Abdollahi, *Food Chem*. **2005**, 93, 293-296.

6- S.M. Praveena, N.A. Omar, *Food Chem.* **2017,** 235, 203-211.

7- M. Soylak, S. Saracoglu, M. Tuzen, D. Mendil, *Food Chem.* **2005**, 92, 649-652.

8- H.S. Ibrahim, M.A. Ibrahim, F.A. Samhan, *J. Hazard. Mater*. **2009a**, 1012-1016.

9- N. Jalbani, T.G. Kazi, N. Kazi, M.K. Jamali, M. B. Arain, *Ren. Fail.* **2008**, 30, 737-745.

10- H.I. Afridi, T.G. Kazi, M.K. Jamali, G.H. Kazi, M.B. Arain, N. Jalbani, G.Q Shar, *Spectrosc Lett.* **2006**, 39, 203-214.

11. Hana R. Alzahrani, Hope Kumakli, Emmanuel Ampiah, Tsdale Mehari, Austin J. Thornton b, Carol M. Babyak, Sayo O. Fakayode. Arabian Journal of Chemistry (2017) 10, 906-913.

12. Abimannan Arulkumar, Sadayan Paramasivam, Rajendran Rajaram, Marine Pollution Bulletin, 119, (1) 2017, 454-459.

13- N. Jalbani, T.G. Kazi, H.I. Afridi, M.B. Arain, *Pak. J. Anal. Environ. Chem.* **2009**, 10 (1 & 2), 48-52.

14- M. Ghaedi, M.R. Fathi, F. Marahel, F. Ahmadi, *Fresen. Environ. Bull*. **2005**, 14, 1158-1163.

15- F. Armagan, M, Soylak, L. Elci, M. Dogan, *J of Trace and Microprobe Tech*. **2002,** 20, 15-27.

16- Tasneem GulKazi, Sham Kumar Wadhwa, Hassan Imran Afridi, Naveed Kazi, Ghulam Abbas Kandhro, Jamil Ahmed Baig, Abdul Qadir Shah, Nida Fatima Kolachi, Muhammad Balal Arain, Journal of Hazardous Materials, 176 (1-3) 2010, 985-991.

17- R.A. Etzel, **2003**. ed. Pediatric environmental health, 2nd ed. Elk Grove Village, IL, American Academy of Pediatrics, 165-180.
18- J. Pronczuk de Garbino, **2004**. ed. Children's health and the environment: a global perspective. Geneva, World Health Organization.
19- WHO. **1992**. Cadmium. Environmental Health Criteria, vol. 134. Geneva: World Health Organization. 1-280.
20- G. Cano-Sancho, G. Perello, M. Nadal, J.L.Domingo, *J. Food Comp. Anal.* **2015**, 42, 71-77.
21- E. Durduran, H. Altundag, M. Imamoglu, S.Z. Yildiz, M. Tuzen, *J. Indus. Eng. Chem.* **2015**, 27, 245-250.
22- P.G. Reeves, R.L. Chaney, *Environ. Res.* **2001**. 85, 215-25.
23- E.M. Gama, AS Lima, VA. Lemos, *J. Hazard. Mater*. **2006**, 136, 757-762.
24- M. Stancheva, L. Makedonski, E. Petrova, *Bulg. J. Agric. Sci.* 19 (Supplement 1), **2013,** 30-34.
25- S.I. Rahlenbeck, A. Burberg, R. D. Zimmermann, *Bull. Environ. Contam. Toxicol*. **1999**, 62, 30-33.
26- N. Jalbani, M. Soylak, *Food Chem***. 2015,** 167, 433-437.
27- D.W. Yap, J. Adezrian, J. Khairiah, B.S. Ismail, R. Ahmad-Mahir, *J. Agricul. Environ. Sci, 2009*, 6 (1), 16-19.
28- EJ. Underwood, **1977**. Trace Elements in Human and Animal Nutrition, fourth ed. Academic Press, New York.
29- M.Smita Achary, K.K. Satpathy, S.Panigrahi, A.K.Mohanty, R.K. Padhi, S. Biswas, R.K. Prabhu, S. Vijayalakshmi, R.C. Panigrahy, *Food Control*, 2016.
30- X.L. Wang, T. Sato, B.S. Xing, S. Tao, *Sci. Total Environ.* **2005**, 350, 28-37.
31- M.L. Huang, S.L. Zhou, B. Sun, Q. G. Zhao, *Sci. Total Environ*. **2008**, 405, 54-61.
32- WHO. **2001**. Safety evaluation of certain food additives and contaminants; Cadmium. WHO Food Additives Series 46. Joint FAO/WHO Expert Committee on Food Additives.
33- World Health Organization WHO. 2003. Summary and conclusion of the 61st meeting of the Joint FOA/WHO Expert Committee on Food Additives (JECFA) JECFA/Sc Rome, Italy 10-19 June, 2013.