



ESTIMATE THE CONTAMINATION BY SOME HEAVY METALS IN SESAME SEEDS AND RASHI PRODUCT THAT AVAILABLE IN LOCAL MARKETS

Raafat A. Abu-Almaaly

Market Researches and Consumer Protection Center, University of Baghdad, Iraq.

Abstract

This study was conducted to estimate the contamination of heavy metals (Arsenic As, Pb, Cadmium Cd, Iron Fe and Cu) in raw sesame samples and Al-Rishi extract from it. For this purpose, 16 samples (8 raw sesame and 8 Rishi products) were collected from 8 local manufactures for the production of Rishi in Baghdad. The Atomic Absorption Spectrometer was used to estimate the concentrations of heavy metals in samples. The results showed significant differences at the level ($P < 0.05$) between concentrations of heavy metals in sesame and Rishi samples, it showed that some samples of raw sesame had concentrations of heavy metals As, Pb, Cd, Fe and Cu were 0.0210, 0.0214, 0.0319, 1.9815 and 1.1002 mg/kg, respectively, some of which were higher than the accepted limits approved by CODEX, all concentrations of heavy metals in the Rishi products higher than in raw sesame reached to 0.1207 and 0.2105, and 0.5232 and 2.9565 and 2.3643 mg/kg, respectively, for the same previous elements, and all of heavy metals concentrations except iron were higher than acceptable limits approved by CODEX, the study showed that the devices and equipment of the sesame extraction in the production of Rashi has caused the transfer of some concentrations of heavy metals from those to the Rashi product.

Key words : heavy metals, sesame, Rashi.

Introduction

Heavy mineral elements are widely found in the crust of the earth, air, water and food, pollution by heavy metal elements is one of the forms of environmental pollution resulting from human agricultural activity, extraction of natural resources and industrialization, because of its toxic, the contamination of food and agricultural crops with heavy metals is a major concern worldwide, while the US Environmental Protection Agency (UEPA) have been listed heavy metals as the most environmentally hazardous contaminants, there are more than 70,000 chemicals in use worldwide and for the level of toxicity, arsenic, cadmium, lead and mercury are in the top rankings in the US list of toxins (ATSDR), which assesses all risks in toxic waste sites based on the severity of the spread and toxicity of those wastes, and the heavy metals that found in the environment can accumulate in the food chain and pose a serious threat to human and animal health (Mehargand Rahman 2003) (Farouk *et al.*, 2011) (Heshmati, 2014) and may lead to serious health problems such as cancer, gastrointestinal and neurological diseases

as well as congenital malformations in the embryos, and causing the death of animals after eating plants and feed containing high concentrations of heavy metals or accumulation in the tissues of animals to cause serious diseases as well as transmission through the food chain to humans (Ciobanu *et al.*, 2012) (Onyedika and Nwosu 2008).

Sesame (*Sesamum indicum* L.) is one of edible seed crops in human and animal food around the world, It belongs to the *Tubiflorae* family and is part of the *Pediaceae* family and is one of the oldest oilseeds cultivated in many countries such as India, Sudan, China and Burma, which are major producers (60% of total global production), it is widely used as food and in preparing food at home and in food processing factories, as it enters the preparation of several types of dishes, salads, sauces and sweets (Bedigian, 2004)(Abou-Gharbia, *et al.*, 2000) (Hassan, 2013). Sesame oil compounds have multiple physiological functions, such as estrogen activation, act as anti-inflammatory substances, reduce blood lipid levels, arachidonic acid

levels, increase antioxidant capacity and enhance bioavailability of γ -tocopherol (Hirata, *et al.*, 1996).

Rashi or tahini is a juice of sesame seeds, which is squeezed after cleaning and roasting on the fire, and can be squeezed without baking. Alrashi contains a high percentage of vitamins and minerals important for the health of the body, as well as add to the various foods to increase flavor and taste delicious, Add to the salads such as the chickpeas salad with yoghurt that gives a distinctive flavor of foods, the factors affecting the presence of heavy metals in Rashi product vary, such as the differences between the sesame species used in Rashi production, agricultural land, geographical location and potential contamination of equipment during the manufacturing process, packaging, as well as the characteristics of good manufacturing practices and health practices (GMP / GHP) and the quality assurance system (HACCP) must be applied by food factories (Fahim, *et al.*, 2013) (Acar, 2011).

Atomic Absorption Spectrometer technology is widely used in the estimation of heavy metals such as copper, lead, iron and zinc in food because of the high sensitivity of this technique to the detection of low ratios of metals (Tuzen and Soylak 2009).

As the sesame seeds are grown in Iraq and imported as well as the spread of the factories of Rashi production and the import it also, enters into a lot of food consumed by the Iraqi citizen and the remnants of the manufacture of Rashi enter the animal feed, this study were aimed to collect random samples of raw sesame seeds and the al-Rishi product from different factories in Baghdad and estimate the heavy metal elements (arsenic, lead, cadmium, iron and copper) in these samples.

Materials and Methods

Samples collection

A total of 16 samples of raw sesame seeds and al-Rishi products (8 sesame and 8 Rashi) were purchased from the al-Rishi factories and stores in Baghdad city (from each factory sample of sesame and Rishi sprayed from of the same sesame) according to Table (1), the samples were collected during the period from March to July 2018. The samples were transferred to laboratories of the Market Research and Consumer Protection Center / University of Baghdad and stored in clean glass bottles in the refrigerator until analysis.

Preparation of solutions and glass

All the standard solutions were prepared for the experiment, using deionized water for all the dilutions, nitric acid HNO_3 and HClO_4 were uses, which are

Table 1: Sesame and Rashi product samples.

Rashi Product trade mark	Sample code	Raw Sesame trade mark	Sample code	NO.
Alwadi	T ₁	Alwadi	S ₁	1
Alburj	T ₂	Alburj	S ₂	2
Alsadek	T ₃	Alsadek	S ₃	3
Juan	T ₄	Juan	S ₄	4
Almeezan	T ₅	Almeezan	S ₅	5
Assoffi	T ₆	Assoffi	S ₆	6
Altahoona	T ₇	Altahoona	S ₇	7
Aljazeera	T ₈	Aljazeera	S ₈	8

supplied by (E. Merck, Germany), all the glass tools and bottles were cleaned with nitric acid (10%) then washed twice with non-ionic water and dried well.

Drying and digesting samples

The samples were dried in the drying oven at 80°C until the weight was stable. The samples were cooled, tested for fine powder and kept in clean polyethylene bags until they were digested.

The extraction of heavy metals from sesame and Rashi samples was done using the wet digestion method mentioned by Acar, (2004), taking 1 gram of powdered sample and put in a 250 cm³ flask, then add 20 cm³ of the acid mixture 2: 1 HNO_3 / HClO_4 , heat for 5-10 minutes by placing it on a hot plate, the end of the digestion process is indicated by the conversion of gray fumes from the beaker to white, the beaker were cooled and add a little non-ionic water to avoid the transfer of the elements to and from the filter paper because of the heat and then filter the digestion product with filter paper to a volumetric flask capacity of 50 cm³ and complete the size to the mark with non-ionic water.

Preparation of Calibration Standards

Standard calibration solutions were prepared at the same time and sample preparation method, standard dilutions using nitrates were prepared with concentrations 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1 mg / dcm³.

Determination of heavy metals in samples

Heavy metals, arsenic As, lead Pb, cadmium Cd, iron Fe and cooper Cu were estimated from the product of the filtration process for samples from wet digestion using Shimadzu AA-6200 supplied with ASC 6100 auto sampler atomic absorption spectrometer equipped with acetylene gas and according to the method mentioned Brkljaca, *et al.*, (2013) with standard solutions.

Statistical analysis

The statistical program SAS was used to analyze the results obtained, and the mean differences between

the averages were compared with the least significant difference (LSD) probability ($P < 0.05$), as indicated by SAS (2012).

Results and Discussion

Determination of heavy metals in raw Sesame samples

Table 2 shows the concentrations of heavy metals in raw sesame samples. The results showed significant differences at the level of ($P < 0.05$) between heavy metals in samples, the concentration of arsenic ranged between 0.0031 - 0.0210 mg / kg in the S_5 and S_2 sesame samples respectively, the concentration of this element in 5 samples was equal to or slightly higher than the accepted maximum of 0.01 mg / kg approved by CODEX (2011) for the presence of arsenic in grains and vegetables, arsenic is found in the environment from natural and human sources because of agricultural and industrial activities, it is one of the most toxic heavy metals that has serious effects on plants and animals, threatens human health as it relates to the development of cancers, including lung cancer, liver, bladder and skin (Zhu, *et al.*, 2011), researches of Fahim, *et al.*, (2013), Hassan, (2013) and (Chen, *et al.*, (2010) indicated that arsenic was found to be low to moderate concentrations in sesame samples of 0.0541 mg/kg in Iran, 0.0035 mg/kg in Egypt and 0.0102 mg/kg in China respectively, while high concentrations of arsenic in two studies in Pakistan amounted to 0.1403 mg/kg in some plants, including sesame, which was irrigated with water contaminated with sewage water (Khan and Muhammad 2013) and 0.1537 mg/kg in sesame seeds cultivated near the Factories area in Islamabad (Malik, *et al.*, 2010), arsenic concentrations reached high levels ranging from 0.1258-1.9203 mg/kg in plants and grains grown in the fields on both sides of the highway cars and trucks, particular in some European countries (Pivic, *et al.*, 2013).

The concentrations lead and cadmium metals for the sesame samples under study were 0.0130-0.0214 mg/kg and 0.0121-0.0319 mg/kg, respectively, the concentrations of these two elements in all samples were slightly higher than the acceptable limits (0.01 mg / kg) (CODEX, 2011), the contamination of some crops with lead and cadmium can be closely related to contaminants in irrigation water, soil and pesticides as well as pollution from highways traffic (Igwegbe, *et al.*, 1992), lead and cadmium concentrations were 1.4850 and 1.9503 mg/kg in plants planted near highways in Europe (Pivic, *et al.*, 2013), while low to medium ratios were recorded in cultivated sesame samples of 0.0516 and 0.0156 respectively in Iran (Fahim, *et al.*, 2013) and 0.0134 and 0.0312 mg/kg

Table 2: Concentrations of heavy metals in raw Sesame samples.

Heavy metals mg/kg					Samples
Cu	Fe	Cd	Pb	As	
0.9981	1.9815	0.0210	0.0187	0.0101	S_1
0.7866	1.7812	0.0134	0.0210	0.0210	S_2
0.1988	1.0432	0.0121	0.0154	0.0121	S_3
0.9565	0.1251	0.0319	0.0214	0.0032	S_4
1.0122	0.9211	0.0212	0.0209	0.0031	S_5
1.1002	1.5645	0.0114	0.0130	0.0107	S_6
0.3233	1.0322	0.0213	0.0181	0.0043	S_7
0.8775	1.0978	0.0127	0.0135	0.0130	S_8
0.409 *	0.356 *	0.0281 NS	0.0173 *	0.0107 *	LSD value
2	3	0.1	0.01	0.01	Permissible limits
* ($P < 0.05$), NS: Non-Significant.					

respectively in Egypt (Hassan, 2013), it is an approach to the values that emerged for lead and cadmium in the sesame samples in the current study, lead is a dangerous element that moves from the plant to the body of the consumer through the food chain and it is dangerous because of a cumulative subject, as it causes physiological damage such as mental retardation and lack of vital functions, lead is found in most factories waste, car residues (oils and gasoline), generators using heavy fuel, frequent operating hours and movement of vehicles in the area, and the frequent use of pesticides, which often dump their residues randomly in most areas of the region as well as the dumping of waste cars, batteries and tires indiscriminately in these agricultural lands (Al- Noor, *et al.*, 2016).

Iron and copper are essential elements of the physiological organism system, but when their concentration exceeds the acceptable limits, they cause dysfunction of the body's physiological system and show multiple symptoms and diseases, the concentrations of these two elements in sesame samples under study were recorded values at 0.1251-1.9815 mg/kg and 0.1988-1.1002 mg/kg respectively, all within the acceptable limits approved by CODEX (2011) for the presence of these elements in grains and vegetables, these results were similar to those of Hassan, (2013) in Egyptian sesame samples, iron and copper concentrations reaching to 1.5311 and 1.99315 mg / kg respectively, while iron concentrations were higher than acceptable in studies carried out Khan and Muhammad (2013) in plants that were irrigated with water contaminated with sewage water and in plants planted near highways in Europe. (Pivic, *et al.*, (2013) The iron ratio was 3.5142 and 4.7511 mg/kg, respectively in both studies.

Determination of heavy metals in raw Sesame

samples

Table 3 shows the concentration of heavy metals in the Iraqi Rashi product, the results showed significant differences at the level of ($P < 0.05$) between the heavy metals in the samples, the concentrations of arsenic in the Rashi samples obtained from the corresponding sesame samples were increased in the previous table table 2 with values ranging from 0.0123 to 0.1207 mg/g, which is higher than the accepted limits of 0.01 mg/kg approved by CODEX (2011) for the presence of arsenic in grains and vegetables, Ashraf, (2014) has been pointed out that the concentration of arsenic in sesame oil was 0.0612 mg/kg for crude sesame in 0.0012 mg/kg in a study conducted at Prince Mohammed bin Fahad University in Saudi Arabia, the reason attributed to the contamination of some equipment and supplies of the squeeze sesame by heavy metals, while Min-Kyoung, *et al.*, (2013) found that sesame oil was highly contaminated with arsenic in South Korea of 0.1722 mg/kg.

Table 3: Concentrations of heavy metals in Rashi samples.

Heavy metals mg/kg					Samples
Cu	Fe	Cd	Pb	As	
1.9891	2.1134	0.1007	0.1132	0.0211	T ₁
1.5978	2.7855	0.3102	0.0232	0.1023	T ₂
1.7698	2.1342	0.2911	0.1033	0.1207	T ₃
2.0122	1.9788	0.1125	0.1878	0.0123	T ₄
2.1204	2.9565	0.5232	0.1299	0.0125	T ₅
2.3643	1.5658	0.9015	0.2105	0.1102	T ₆
1.9211	1.7958	0.2441	0.1655	0.0324	T ₇
1.9349	2.0122	0.3411	0.2033	0.0912	T ₈
0.592 *	0.651 *	0.2602 *	0.0512 *	0.0443 *	LSD value
2	3	0.1	0.01	0.01	Permissible limits

* ($P < 0.05$).

The concentrations of lead and cadmium in the Rashi samples under study were higher than in sesame, with values ranging from 0.1033 to 0.2105 mg/kg and 0.1007 to 0.9015 mg/kg respectively, these two elements concentrations in all samples was found to be higher than the acceptable limits of 0.01 mg/kg (CODEX, 2011), these results were similar to those found in Acar, (2011) that the concentration of lead element increased in Rashi samples to 0.2418 mg/kg, the studies of both Ashraf, (2014) in Saudi Arabia and Min-Kyoung, *et al.*, (2013) in South Korea, founded high concentrations of lead and cadmium in sesame oil amounted to 0.1732 and 0.2000 mg/kg respectively, 0.0575 and 0.1093 mg/kg for cadmium respectively in the two studies.

The results in Table 3 showed that concentrations of iron and copper in Rashi product were higher than in raw

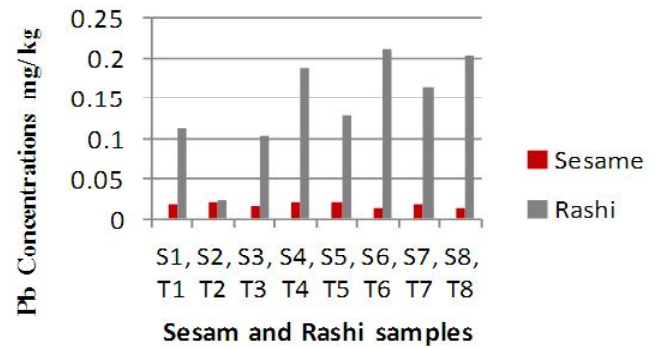


Fig. 1: Comparing Arsenic metal concentrations between raw sesame and Rashi product.

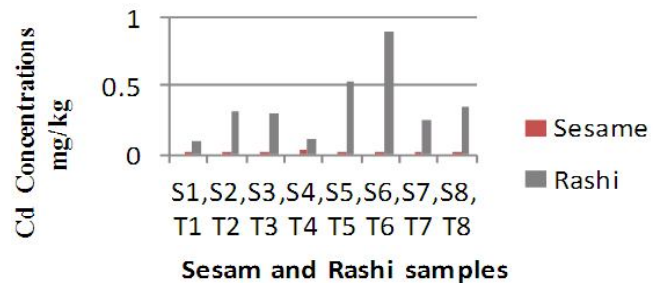


Fig. 2: Comparing Lead metal concentrations between raw sesame and Rashi product.

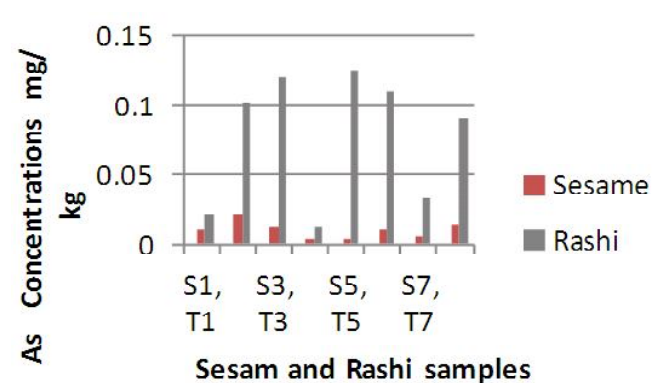


Fig. 3: Comparing Cadmium metal concentrations between raw sesame and Rashi product.

sesame, but, iron concentrations, ranging from 1.5658 to 2.9565 mg/kg in Rashi samples under study, remained within the acceptable limits of 3 mg/kg CODEX, (2011), copper concentration in T₄, T₅ and T₆ was 2.0122, 2.1204 and 2.3643 mg/kg respectively, there was higher than the acceptable limit (2 mg/kg), while remaining in the other Rashi samples within acceptable limits, the results were identical to those found in El-Adawy and Mansour (2000) in Egypt that the concentrations of iron and copper in Rashi samples were higher than in sesame, reaching 2.0331 and 2.0211 mg/kg respectively for the two elements, while the concentrations of the two elements were significantly higher in Turkey’s Rashi samples (Acar, 2011) reaching 5.3631 and 6.8332 mg/kg respectively, This was attributed to the pollution of the Rashi product from the systems and devices of the squeeze, which

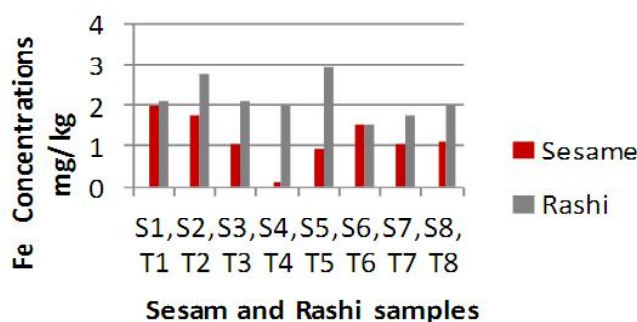


Fig. 4: Comparing Iron metal concentrations between raw sesame and Rashi product.

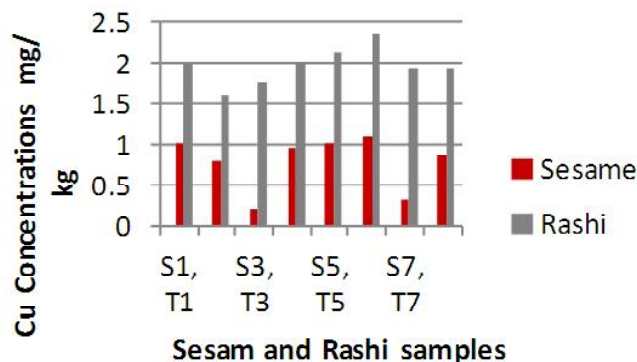


Fig. 5: Comparing Copper metal concentrations between raw sesame and Rashi product.

contains high concentrations of minerals.

When comparing the samples of raw sesame and the Rashi product based on the study results and each trade mark separately (as shown in Figures 1, 2, 3, 4 and 5), it is clear that the concentrations of heavy metals in the Rashi product are much higher than in the raw sesame before the production of the squeeze, some studies have attributed the contamination to the metal equipment used in the preparation, roasting and sesame- squeezing process, which can be old, rusty and of poor quality, may therefore be the biggest cause of product contamination by heavy metal (Acar, 2011) (El-Adawy and Mansour 2000).

References

- Abou-Gharbia, H.A., A.A.Y. Shehata and F. Shahidi (2000). Effect of processing on oxidative stability and lipid classes of sesame oil. *Food Research International*, **33**: 331-340.
- Acar, O. (2004). Determination of lead, copper, manganese and zinc in botanic and other biological samples by electrothermal atomic absorption spectrometry using scandium-containing chemical modifiers. *Analytica Chimica Acta*, **526**: 103-109.
- Acar, O. (2011). Determination and Evaluation of Copper, Lead, Iron and Zinc Contamination Levels in Cheese and Tahini Halva by Atomic Absorption Spectrometry. *Internet Journal of Food Safety*, **13**: 45-53.
- Al- Noor, T.H., L.K. Aslan and L.J. Abd-Ali (2016). Estimation of heavy metals in the water, 'plants and soils adjacent to agricultural areas of the waters of the Tigris river in Al-Grea't-Baghdad-Iraq region. *Journal for Natural and Engineering science*, **4(7)**:17-35.
- Ashraf, M.W. (2014). Health Risk Assessment of Selected Heavy Metals in Seven varieties of Vegetable Oils consumed in Kingdom of Saudi Arabia. *Journal of the Chemical Society of Pakistan*, **36(4)**: 691-698.
- Bedigian, D. (2004). History and lore of sesame in H. Attia, 2007. Quality characteristics of sesame seeds southwest Asia. *Economic Botany*, **58(3)**: 329-353.
- Brkljaca, M., J. Giljanovic and A. Prkic (2013). Determination of Metals in Olive Oil by Electrothermal Atomic Absorption Spectrometry: Validation and Uncertainty Measurements. *Analytical Letters*, **46(18)**: 1-34. DOI: 0.1080/00032719.2013.814056.
- Chen, Z.F., Y. Zhao, Y. Zhu, X. Yang, J. Qiao, Q. Tian and Q. Zhang (2010). Health risk of heavy metals in sewage-irrigated soils and edible seeds in Langfeng of Hebei Province. *China Journal of the Science of Food and Agriculture*, **90(2)**: 314-320.
- Ciobanu, C., B.G. Slencu and R. Cuciureanu (2012). Estimation of dietary intake of cadmium and lead through food consumption. *Revista medico-chirurgicala a Societatii de Medici si Naturalisti din Iasi*, **116(2)**: 617-623.
- Codex committee on contaminants in foods. (2011). Maximum Levels for Contaminants and Toxins in Foods, Part I, Fifth Session, CF/5 INF/1 March 2011.
- El-Adawy, T.A and E.H. Mansour (2000). Nutritional and physicochemical evaluations of tahina (sesame butter) prepared from heat treated sesame seeds. *Journal of the Science of Food and Agriculture*, **80**: 2005-2011.
- Fahim, N.Kh., H.R. Beheshti, S.F. Janati and J. Feizy (2013). Survey of cadmium, lead, and arsenic in sesame from Iran. *International Journal of Industrial Chemistry*, **4**:10.
- Farouk, S., A.A. Mosa, A.A. Taha, H.M. Ibrahim and A.E. Gahmery (2011). Protective effect of humic acid and chitosan on radish (*Raphanus sativus*, L. var. *sativus*) plants subjected to cadmium Stress. *Journal of Stress Physiological Biochemistry*, **7(2)**: 99-116.
- Hassan, M.A.M. (2013). Studies on Egyptian Sesame Seeds (*Sesamum indicum* L.) and its Products. 2. Effect of Roasting Conditions on Peroxide Value, Free Acidity, Iodine Value and Antioxidant Activity of Sesame Seeds (*Sesamum indicum* L.). *World Journal of Dairy & Food Sciences*, **8(1)**: 11-17. DOI: 10.5829/idosi.wjdfs.2013.8.1.1114
- Heshmati, A. (2014). Evaluation of Heavy Metals Contamination of Unrefined and Refined Table Salt. *International Journal of Research Studies in Biosciences*, **2 (2)**: 21-24.
- Hirata, F., K. Fujita, Y. Ishikura and K. Hosoda (1996). Hypocholesterolemic effect of sesame lignan in humans.

- Atherosclerosis*, **22**: 135-136.
- Igwegbe, A.O., H. Belhaj, T.M. Hassan and A.S. Gibali (1992). Effect of a Highway'S traffic on the level of lead and cadmium in fruits and vegetables grown along the roadsides. *Journal of Food Safety*, **13(1)**: 7-18.
- Khan, M.U., R.N. Malik and S. Muhammad (2013). Human health risk from Heavy metal via food crops consumption with wastewater irrigation practices in Pakistan. *Chemosphere*, **93**: 2230-2238.
- Malik, R.N., S.Z. Husain and I. Nazir (2010). Heavy metal contamination and accumulation in soil and wild plant species from industrial area of Islamabad, Pakistan. *Pakistan Journal of Botany*, **42**: 123-127.
- Meharg, A. A and M. Rahman (2003). Arsenic contamination of Bangladesh paddy soils: Implications for rice contribution to arsenic consumption. *Environmental Science and Technology*, **37**: 229-34.
- Min-Kyoung, P., Y. Ji-Hyock, L. Je-Bong, I. Geon-Jae, K. Doo-Ho and K. Won-Il (2013). Detection of Heavy Metal Contents in Sesame Oil Samples Grown in Korea Using Microwave-Assisted Acid Digestion. *Journal of Food Hygiene and Safety*, **28(1)**: 45-49.
- Onyedika, G.O. and G.U. Nwosu (2008). Lead Zinc and Cadmium in Roots Crops from Minerized Galena- Sphalerite Mining Areas and Environment. *Pakistan journal of Nutrition*, **7(3)**: 418-420.
- Pivic, R.N., A.B.S. Sebic and D.L. Josic (2013). Assessment of soil and plant contamination by select heavy metals along a major European highway. *Polish Journal of Environmental Studies*, **22**: 1465-1472.
- (SAS) Statistical Analysis System (2012). User's Guide. *Statistical*. Version 9.1th ed., SAS. Inst. Inc. Cary. N.C. USA.
- Tuzen, M. and M. Soylak (2009). Investigation of the levels of some element in edible oil samples produced in Turkey by atomic absorption spectrometry. *Journal of Hazardous Materials*, **165**: 724-728.
- Zhu, F., W. Fan, X. Wang, L. Qu and S. Yao (2011). Health risk assessment of eight heavy metals in nine varieties of edible vegetable oils in China. *Food and Chemical Toxicology*, **49**: 3081-3085.