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ORIGINAL ARTICLE

Monitoring and Risk Characteristics of Heavy Metals in Agricultural Products in Qom, Iran

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KEYWORDS

Heavy Metals;
Monitoring;
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ABSTRACT: Considering the high consumption of agricultural and greenhouse fruits in the city of Qom, and the lack of study records, this research for monitoring of Heavy metals in agricultural and greenhouse products and conduct of human health risk assessment was carried . This study was designed and conducted in two stage. In the first stage, two categories' of agricultural products including vegetables (lettuce, tomatoes, onion and potatoes) and greenhouse products (cucumbers, tomato, bell pepper) were selected and after sample preparation and extraction, the amounts of heavy metals was measured with the atomic absorption device. In the second stage, exposure risk assessment of heavy metals (Pb, Cd, Cr, Hg, and As) were investigated. The finding of the research revealed that the measured concentrations of heavy metals in agricultural products as well as greenhouse products compared to the maximum allowed values of heavy metals in agricultural products in the Iranian Standards Institute are higher in 35% of the evaluated samples. Health risk assessment results of this study indicated that hazard index (HI) for agricultural and greenhouse products is lower than 1(HI <1), therefore, it is estimated that the non-cancer risk of consuming these products is negligible according to the exposure pattern and consumption level. Moreover, the cancer risk (Σ CR) calculated for age groups of childhood (1-6) by consumption of onion, tomato and lettuce products was higher than the estimated acceptable limits (the acceptable level of 1 case per 100000). Considering the wide trend of using agricultural products in Iran and especially in the city of Qom, as well as the risk of carcinogenesis is higher than the acceptable limits, Continuous monitoring of heavy metal levels in products as well as in water and soil resources used in crop cultivation is inevitable.

INTRODUCTION

The quality of agricultural and food products is the primary health indicator for societies. However, the quality of agricultural products has been threatened in recent decades due to the indiscriminate use of herbicides, toxins, pesticides, and hormones, which has led to increased mortality rates and the reduction of the average life expectancy of the world's population due to the emergence of various diseases and heightened environmental pollution [1]. Contamination of soil and agricultural crops by toxic elements due to the progress of industries as well as the lack of proper use of chemical fertilizers and livestock in agricultural lands has raised significant concerns about the quality and safety of these products and their impact on human health.

Every year, thousands of tons of toxic compounds enter the soil through different pathways. Heavy metals as one of the most dangerous toxic compounds in the soil and agricultural products have posed danger to the health of consumers [2,3]. The relationship between short-term and long-term exposure to heavy metals through food

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and the health risks, including carcinogenesis, has been widely studied and proven. In a study by Setia Budi on the source, toxicity and carcinogenic health risk assessment of heavy metals, it was reported that the consequences of exposure to heavy metals depend on a number of factors, including pathway and duration of exposure, dosage, and chemical species, as well as age, sex, genetics, and nutritional behavior of the consumer [4].

Bioaccumulation of heavy metals through the food chain, leading to increased concentration, can be harmful to human health. Some heavy metals, such as copper, zinc, and cobalt, are necessary in appropriate amounts for most biological systems, while others such as lead, arsenic, and cadmium are toxic to animals, plants, and humans [5]. Cadmium is known as a carcinogenic substance that is a major contributor to most cancers. It also seems to be implicated in causing heart diseases and blood pressure. In addition, by affecting the blood and kidney systems, it causes metabolic abnormalities and neuro-physical defects in children. Heavy metals lead, cadmium, and chromium are well-known carcinogenic elements linked to various cancers, especially gastrointestinal cancer [6]. The Iranian Standard and Industrial Research Institute has determined the maximum permissible limits of these elements in food and agricultural products under standard number 12968. Considering the high consumption of agricultural and greenhouse products in the city of Qom, as well as the lack of study records, this research was carried out to survey the concentrations of heavy metals in agricultural and greenhouse products and conduct the exposure risk assessment process [7].

MATERIALS AND METHODS

Design of study

This study was conducted in two stage in the Qom city as a large city located in the center of Iran with the approximately 1250,000 habitants. In the first stage, two categories' of agricultural products including fruits (tomatoes , lettuce, , onion and potatoes) and greenhouse products ((cucumbers, tomato, bell pepper) were selected and collected from the main Fruit and Vegetables Supply Center and greenhouse sites that located in the Jafarabad, Tagharud and Jamkaran of Qom province (Figure1). In this study, the sample size was estimated according to the literature and the formula n = $Z_{1-a}\,^{2}*P\ (1-P)/d^{2}$. A confidence interval of 95% (Z1-a), test accuracy of 5% (d), and P = 54% were considered. A total of 170 vegetable samples, including lettuce (n = 25), tomato (n = 30), onion (n = 20), potato (n = 35), greenhouse cucumbers (n = 20), greenhouse tomato (n = 20), and greenhouse bell pepper (n = 20), were analyzed in order to assess the levels of heavy metals (each sample weighed 1 kg). In the second stage, exposure risk assessment of heavy metals (Cd, Pb, Cr, Hg, and As) was conducted by determining daily intake through vegetables.

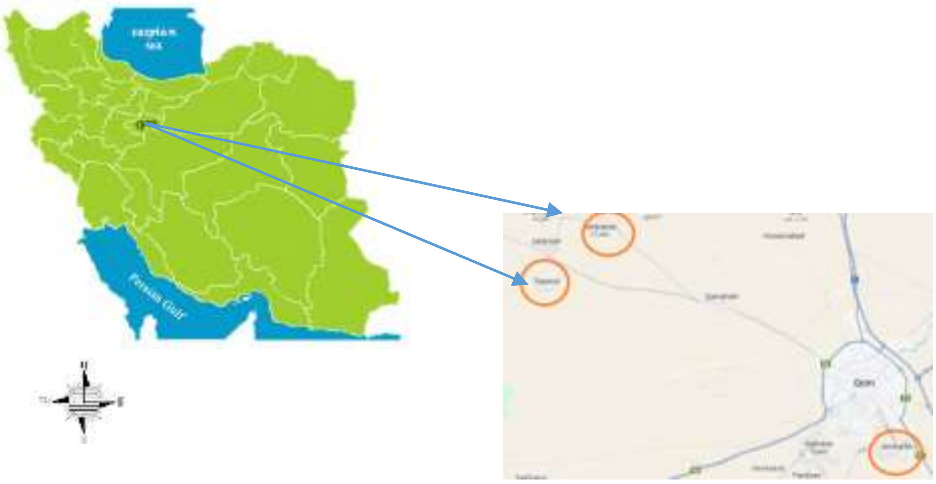

Figure 1. Map of study area.

Chemicals and reagents, preparation of samples, and method validation

During sample preparation, non-edible parts were separated, and then the samples were washed and frozen. For this purpose, about 200 ± 2 g of each sample was dried, crushed, homogenized, and prepared using a freeze dryer (the drying process was performed at 80°C for 24 h). Afterward, 10 g of the selected and crushed samples were washed with distilled water and placed in an electric dryer at 70°C for 72 h until a constant weight was achieved. To obtain the plant extract, 1 g of the dry plant sample was ashed in a Chinese plant for 2 h at a temperature of 550°C in an electric furnace. After adding 10 mL of 2 M HCl, the samples were slowly heated on a heater and the filtered extract was collected in a 50-mL flask.

After the extraction process, heavy metals concentration (Cd, Pb, Cr, As, Hg) in the product extract is measured with the atomic absorption device (model PG990) by PG Instrument Company and by the furnace method. In order to ensure the correctness of the method, the validation of the method in terms of accuracy, repeatability, accuracy is also examined. The method fitted in this research is a linear model with (R2= 0.974) and limit of detection (LOD) 0.01 mg/l was calculated as (Figure 2) [8].

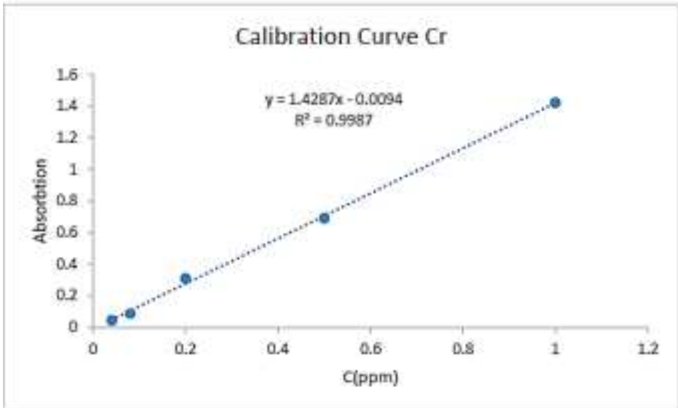

Figure 2. Calibration curve of Cr.

Exposure risk assessment

Methods of risk assessment for agricultural products consumption, according to the process of United States

Environmental Protection Agency (US EPA) was applied, the formula components defined as follows

EDI= (C× C_{factor} ×IR×FI×EF×ED)/ (BW×AT) (1)

EDI: amount of daily contaminant intake

C: concentration of contaminants in food gday-1

C_{factor}: conversion factor to convert fresh vegetable weight to dry weight

IR: daily nutritional pattern (g day^{-1}) that in this research, based on information about the amount of agricultural products consumption in the household food basket was received from theInstitute of Nutritional Research and Food Industries of Iran, consumption of onions was 36 $gday^{-1}$, lettuce 14 gr/day, tomatoes 42 g day^{-1} and potatoes 60 $gday^{-1}$, greenhouse cucumbers50 g day^{-1}, greenhouse tomatoes 40 gr/day, greenhouse bell pepper 5 g day^{-1} were considered. Also, Based on the data gathered from among the respondents in the study population , the frequencies of consumption in the household food basket: lettuce 2 times a month, onion 3 times a week, potato 3 times a week , tomato 2 times a week, greenhouse cucumbers 2 times a month and greenhouse bell pepper Once a month were estimated.

FI = Bioavailability absorption of heavy metals that this coefficient for worst scenario 0.4 were considered [9, 10].

EF = exposure frequency (365 day/year)

ED: Number of years that products is used and with regard to the age range in this study including Childhood (1 -6) and adults (36-55)

BW = Body weight, for age groups which in this study is considered 65 kg for adults and 15 kg for children [11].

AT: average life time (ED×365 days/years)

In order to deterministic risk assessment (Non-Cancer effects) hazard quotient (HQ) was estimated through Eq.2:

$$HQ = \frac{EDI}{RfD} \qquad (2)$$

The values of RfD (mg/kg/day) for heavy metals including 3.6E-3, 3E-3, 3E-4, 1E-3, and 3E-4 for Pb, Cr, As, Cd and Hg were considered respectively.

In HQ <1.0 indicated that no significant risk and HQ >1.0 shows significant risk for human health [10]. Hazard index (HI), which is obtained by summing the HQ values, are determined by Eq.3:

$$HI = \Sigma HQ \qquad (3)$$ [8].

Cancer risk assessment (CR) of heavy metals, using the Incremental Lifetime Cancer Risk (ILCR) were calculated (Eq.4).

$$ILCR = \text{intake (mg/kg BW/day)} \times CSF \qquad (4)$$

CSF: cancer slope factor value (mg/kg bw/day) of Pb, Cr, As, Cd and Hg 0.0085, 0.5, 1.5, 0.38, 0.0003 were determined respectively [12, 13]. In this study for cancer risk, acceptable lifetime cancer risk for heavy metals $10^{-6} < ILCR < 10^{-4}$ were considered.

Required data for exposure risk assessment were gathered by structured and approved questionnaire (NUTRIKAP) through interviews with 1000 people who were responsible for providing basic materials and food in the family.

[14]. The reliability and validity of the questionnaire were confirmed by nutritional experts in health centers. The sampling method at the household level was the single stage cluster sampling (20 clusters of 50 people in Qom Province).

RESULTS

Quantity of heavy metals concentration in the vegetables

The concentrations of **heavy metals** in groups of vegetables samples are presented in Table 1, Figures 3 and Figure 4 .

Table 1. Heavy metals concentrations (mg/kg) in the examined samples.

Samples characteristics	Pb	Cd	Cr	Hg	As
Potato	0.23±0.02	0.058 ±0.012	0.034±0.015	0.61±0.20	0.042±0.01
Tomato	0.15±0.017	0.04±0.012	0.038±0.001	0.37±0.01	0.39±0.012
Onion	0.33±0.01	0.08±005	0.03±0.001	0.56±0.21	0.047±0.002
Lettuce	0.3 ± 0.11	0.045 ± 0.023	0.064 ± 0.01	0.49 ± 0.15	0.07±0.01
Green house cucumbers	0.25±0.002	0.039±0.007	0.45±0.009	0.05±0.008	0.005±0.001
Green house tomato	0.016±0.008	0.006±0.001	0.005±0.001	0.4±0.1	0.09±0.001
Green house bell pepper	0.3±0.07	0.35±0.02	0.047±0.001	0.7±0.1	0.067±0.001

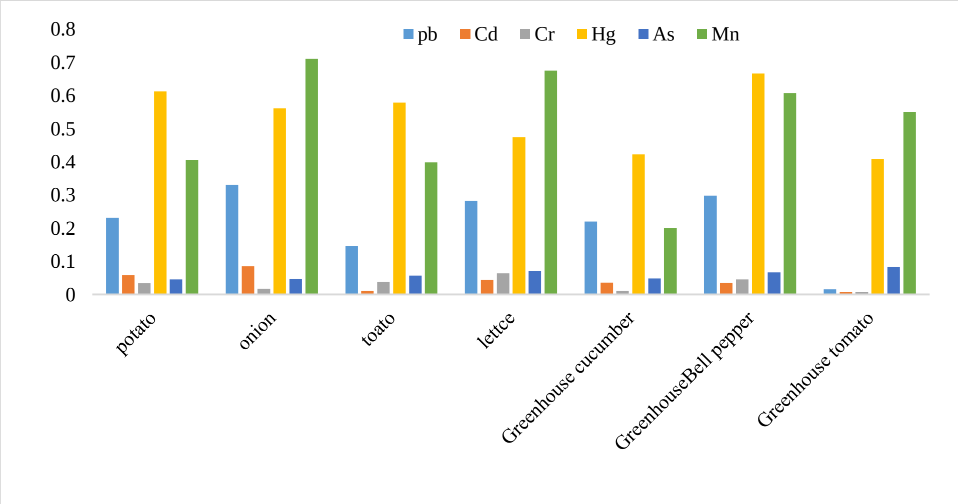

Figure 3. The concentration of heavy metals in each of the agricultural products

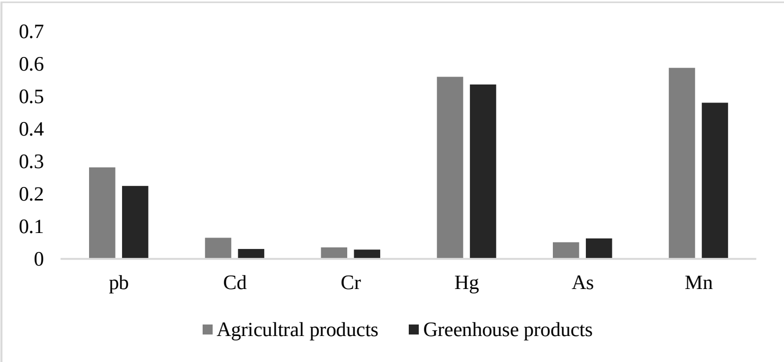

Figure 4. Comparative diagram of heavy metal concentration in agricultural and greenhouse products

Exposure and health risk assessment

In this study, according to the steps of a health risk assessment process, the results are shown in Tables (2, 3 and 4).

Table 2. Estimated daily intake (mg/kg bw/day) of food products in age groups

Age groups (year)	Type of food products	Food products	Pb	Cd	Cr	Hg	As
Childhood (1 -6)	Agricultural Products	potato	13E-6	37E-7	18E-7	33E-6	2E-6
		onion	98E-7	17E-7	6E-7	15E-6	9E-7
		tomato	4E-6	14E-7	14E-7	14E-7	13E-6
		lettuce	41E-7	13E-6	13E-6	65E-8	8E-7
	Green house products	cucumber	7E-6	1E-6	7E-7	1E-6	1E-7
		bell pepper	8E-7	7E-7	9E-9	18E-8	13E-9
		tomato	1E-7	6E-8	4E-8	44E-7	8E-7
Adults (36-55)	Agricultural Products	potato	27E-7	7E-7	3E-7	7E-6	5E-7
		onion	6E-7	18E-8	18E-8	18E-8	18E-8
		tomato	9E-7	36E-7	17E-8	2E-6	3E-6
		lettuce	35E-8	51E-9	66E-9	6E-7	71E-9
	Green house products	cucumber	32E-7	48E-7	54E-7	6E-7	6E-7
		bell pepper	2E-7	2E-7	3E-8	56E-6	6E-7
		tomato	5E-7	22E-9	17E-9	16E-7	28E-8

Table 3. Hazard quotiet for age groups from vegetables consumption in Qom province.

Age groups (year)	Type of food products	Food products	Pb	Cd	Cr	Hg	As	HI (Σ HQ)
Childhood (1 -6)	Agricultural Products	potato	35E-4	37E-4	6E-4	82E-3	66E-4	96E-3
		onion	27E-4	17E-4	2E-4	5E-2	3E-3	57E-3
		tomato	11E-4	14E-4	46E-5	46E-4	43E-3	5E-2
		lettuce	11E-4	13E-3	43E-4	21E-4	26E-4	23E-3
	Green house products	cucumber	19E-4	1E-3	23E-5	33E-4	33E-5	67E-4
		bell pepper	22E-5	7E-4	3E-6	6E-4	43E-6	15E-4
		tomato	19E-5	6E-5	23E-6	14E-3	26E-4	16E-3
Adults (36-55)	Agricultural Products	potato	75E-5	7E-4	1E-4	23E-3	16E-4	26E-3
		onion	16E-5	18E-5	6E-5	6E-4	6E-5	1E-3
		tomato	25E-5	36E-4	6E-5	56E-5	1E-2	14E-3
		lettuce	97E-6	51E-6	22E-6	22E-5	23E-5	62E-5
	Green house products	cucumber	86E-5	48E-4	18E-4	23E-4	2E-3	11E-3
		bell pepper	19E-5	2E-4	1E-5	18E-2	2E-3	18E-2
		tomato	13E-5	22E-6	56E-7	53E-4	93E-5	63E-4

Table 4. Cancer risk of **heavy metals** for age groups from vegetables consumption in Qom province.

Age groups (year)	Type of food products	food products	Pb	Cd	Cr	Hg	As	(Σ CR)
Childhood (1 -6)	Agricultural Products	potato	13E-8	14E-7	9E-7	99E-10	3E-6	54E-7
		tomato	83E-9	64E-8	3E-7	45E-10	13E-6	14E-6
		onion	34E-8	53E-8	7E-7	42E-10	19E-6	26E-6
		lettuce	34E-8	49E-7	65E-7	2E-10	12E-7	13E-6
	Green house products	cucumber	59E-9	38E-8	45E-10	3E-10	15E-8	11E-8
		tomato	6E-9	26E-8	2E-8	5E-10	19E-9	3E-7
		bell pepper	9E-10	22E-9	15E-8	3E-10	12E-7	1E-7
Adults (36-55)	Agricultural Products	potato	23E-9	26E-8	33E-9	21E-10	75E-8	1E-6
		tomato	51E-10	68E-9	9E-8	5E-10	27E-8	4E-7
		onion	77E-10	2E-7	80E-9	6E-10	45E-7	13E-7
		lettuce	3E-9	19E-7	33E-9	2E-10	10E-9	19E-7
	Green house products	cucumber	27E-9	18E-7	27E-7	2E-10	9E-7	54E-7
		tomato	17E-10	7E-8	15E-9	16E-9	9E-7	1E-6
		bell pepper	43E-10	84E-8	85E-10	5E-10	42E-8	12E-7

DISCUSSION

In the present study, concentrations of heavy metals (Pb, Cd, Cr, Hg, and As) were investigated in seven agricultural products (potatoes, tomatoes, onions, lettuce, greenhouse cucumbers, greenhouse tomatoes, and greenhouse bell peppers). According to the results, the following concentrations were detected: 0.23 ± 0.02, 0.058 ± 0.012, 0.034 ± 0.015, 0.61 ± 0.20, and 0.042 ± 0.01 mg kg^{-1} for Pb, Cd, Cr, Hg, and As, respectively. The highest concentrations of Pb, Cd, Cr, Hg, and As were detected in onions, greenhouse bell peppers, greenhouse cucumbers, potatoes, and tomatoes, respectively (Table 2). The results of the study revealed that the measured concentrations of heavy metals exceeded the maximum permissible limits of heavy metals in agricultural products set by the Iranian Standards Institute in 35% of the analyzed agricultural and greenhouse products. According to the findings of the study, Pb levels in cucumbers and bell peppers, Cd levels in tomatoes, and Hg levels in potatoes, tomatoes, onions, and lettuce samples were reported to be above the permissible limits set by the Iranian Standards Institute. Health risk assessment indicated that the hazard index (HI) for agricultural products was lower than 1 (HI < 1); therefore, it is estimated that the non-cancer risk of consuming these products is negligible according to the exposure pattern and consumption levels. The highest HI value was found in tomatoes (0.05) for children aged 1–6 years.The results of cancer risk assessment presented in Table 4 indicated that the mean cancer risk calculated for children aged 1–6 from the consumption of onions, tomatoes, and lettuce products was higher than the estimated acceptable limits (the acceptable level of 1 case per 100,000). The qualitative descriptor for these cancer risk values represents a concern for increased cancer risk in this age group with the daily intake of heavy metals from agricultural products. Similar to the present study in Iran, several other studies have also emphasized the health risks associated with exposure to heavy metals in food [15, 16]. In a study by Arfaeinia et al., concentrations of heavy metals in agricultural products in Dayyer City were investigated, and the results showed that the levels of heavy metals in crops irrigated with water mixed with urban sewage were significantly higher than those irrigated with groundwater [17]. The concentrations of heavy metals in the present study were much lower for all products compared to those in the study by Arfaeinia. The findings of the present study are consistent with those of the study by Zafarzadeh et al., who assessed the health risks of heavy metals in vegetables in Northeastern Iran. The results indicated that although Cd and Pb concentrations in cucumbers and tomatoes were lower than the maximum permissible limit for vegetables, Pb posed significant non-carcinogenic risks, and Cd was of concern due to its carcinogenic potential [18].Another similar study carried out by Kharazi in Hamadan investigated the levels of heavy metals in food crops and conducted human health risk assessment. The results of the study revealed that the non-carcinogenic risk of As (HQ > 1.0) and the carcinogenic risks of As and Cd were higher than the safe levels in children (1×10^{-6}) [19].The results of the study by Adedokun et al. on the health risks of heavy metals via the consumption of some leafy vegetables in Lagos Metropolis revealed that the target hazard quotient (THQ) in Pb, Cd, and Cr is less than 1 in all the vegetable species; therefore, it does not pose serious health risks. Although the concentrations of all heavy metals (Pb, Cd, and Cr) in the study by Adedokun et al. are higher than those in the present study, due to the level of exposure, their results have similarities with the results of the present study [20].In the study by Sultana et al. on health risk assessment for heavy metal exposures from consuming vegetables, the results indicated that the probability of developing cancer from vegetable consumption exceeded the US-EPA threshold risk limit (>10−4) for As and Cd, which is not in line with the results of the present study [21]. However, Amerian’s study on the risk assessment of heavy metal consumption through greenhouse crops in Kermanshah County in the west of Iran showed that the risk index for heavy metals was below 0. 1, which confirms the results of the present study [22].By analyzing the results of studies conducted on the risk assessment of exposure to heavy metals in food products, it has been found that in addition to the concentration of heavy metals, their daily intake is also of great importance. [23].Overall, the key aspect in all studies related to the monitoring and evaluation of health risks caused by exposure to heavy metals in agricultural products was the residual amount and exposure to these products based on nutritional and behavioral patterns as well as the cultural and economic characteristics of the communities [23].

CONCLUSIONS

Considering the extensive use of agricultural products in Iran, especially in the city of Qom, and since the carcinogenic risk is higher than the acceptable limits, it is essential to continuously monitor heavy metals during cultivation and the storing of products at the distribution levels.

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ETHICAL CONSIDERATION

This project has approved with ethical code IR.MUQ.REC.1401.161

Conflict of interest

Authors declare that he has no conflict of interest.

Author contributions

All authors accept public responsibility for the substance of the material submitted for publication, author contributions: Ahmad Reza.Yari and Rahim Aali, data collection, Yadollah.Ghafuri, study conception and design.

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