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# Essential elements in the different types of fruits, soil, and water samples collected from Markazi province, Iran: a health risk assessment study

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## Abstract

Fruits could contain elements in various concentrations, which can have both positive and negative impacts on human health. The concentrations of essential elements, including Iron (Fe), Copper (Cu), Zinc (Zn), Manganese (Mn), and Chromium (Cr) in five types of fruits, namely, peach, apple, grape, nectarine, and golden plum, and the soil and irrigation water from six industrial zones of Markazi province, Iran, were evaluated using an inductively coupled plasma-optical emission spectroscopy (ICP-OES) technique. The noncarcinogenic risk was assessed by determining the target hazard quotient and the Monte Carlo simulation model. The highest concentrations of Fe, Mn, and Cr were observed in golden plum, while the highest concentrations of Cu and Zn were noted in grape and apple, respectively. The order of the mean of concentrations of elements in the soil and water samples were Fe > Mn > Zn > Cu > Cr. The transfer factor (TF) results indicate that studied fruits could not absorb a high amount of these elements from the soil (TF < 1). Target hazard quotient values of these elements in both adults and children were ranked as Cr > Cur > Fe > Mn > Zn. The target hazard quotient was 95% and total target hazard quotient was <1, meaning that the consumption of fruits is safe for consumers.

*Keywords*: essential elements; food safety; fruits; health risk assessments; nutritional assessment

## Introduction

Fruits have been recognized as one of the most important components of diet owing to their valuable content of different nutrients, such as minerals, vitamins (mainly C and A), antioxidants, water, polysaccharides, sugars, and fibers (Grembecka and Szefer, 2013). In this regard, it has been suggested that at least 400 g of fruits and veggies should be consumed as part of daily diet to maintain good health and prevent diseases (WHO, 2018). The intake of fruits and vegetables is inversely associated with the incidence of chronic disease, hypertension, diabetes, cataracts, cancers, and cardiovascular diseases (Prakash *et al.*, 2012). Fruits could contain essential and nonessential elements in varying concentrations, which in turn can impact human health (Wang *et al.*, 2015).

Microelements like Iron (Fe), Copper (Cu), Zinc (Zn), Manganese (Mn), and Chromium (Cr) are essential for several biochemical and physiological pathways (Bagdatlioglu *et al.*, 2010). In addition, these elements are crucial for lipids and carbohydrates metabolism, as well as the synthesis of proteins (Grembecka and Szefer, 2013). Some elements found in fruits offer strong antioxidant activity, and they can act as a cofactor of antioxidant enzymes such as superoxide dismutase (Cu, Zn-SOD, Mn-SOD), glutathione peroxidase (Se), and catalase (contains four porphyrin heme [Fe] groups) (Sajib *et al.*, 2014).

Fe, as a very abundant essential element on the Earth, plays a vital role in the body (Abbaspour *et al.*, 2014). It binds to the proteins like hemoproteins, heme enzymes, and nonheme compounds such as transferrin and ferritin (carrier proteins of Fe). The significant part of Fe in the soil is insoluble and not available for plants. The consumption of cereals, fruits, legumes, and vegetables can provide the required amounts of nonheme Fe (Trumbo *et al.*, 2001). In this regard, the shortage of Fe in the diet is a significant contributor to anemia, which is a well-known health issue in many countries (Abbaspour *et al.*, 2014), including Iran (Akbari *et al.*, 2017).

On the contrary, the intake of Fe in a high dose could have some adverse effects on the gastrointestinal system, which can result in cardiovascular disease (Korkmaz *et al.*, 2019b; Trumbo *et al.*, 2001), Parkinson's disease, Alzheimer's disease, and type-2 diabetes (Korkmaz *et al.*, 2019b). Cu is a cofactor for various enzymes and also has several functions in the immune system, antioxidant defense, and neuropeptide synthesis (Prohaska and Lukasewycz, 1990). Cu deficiency can cause impaired development in the cardiovascular system, bone malformation, ongoing neurologic and immunologic abnormalities, and also an alteration in cholesterol metabolism in adults (Bost *et al.*, 2016). On the contrary, excessive intake of Cu has adverse effects on the gastrointestinal tract and liver (Scheinberg and Sternlieb, 1996) and also causes kidney disorders (Korkmaz *et al.*, 2019a) such as Wilson's disease (Trumbo *et al.*, 2001). Zn is one of the essential microelements in all stages of life, especially during pregnancy and infancy (McArdle and Ashworth, 1999). It promotes healthy growth and stimulates the activity of more than 100 enzymes, carbohydrate metabolism and growth, and the development of the fetus. Zn deficiency causes a decrease in nerve conduction, mental lethargy, neurosensory disease, skin lesions, acrodermatitis, infertility, and hypogonadism (Brown *et al.*, 2001). Mn is crucial in the formation of bones, connective tissues, amino acids, carbohydrates, and lipid metabolism. However, exposure to high levels of Mn causes some adverse effects on the nervous system (Araújo *et al.*, 2019; Horning *et al.*, 2015). Cr aids in glucose, proteins, and lipids metabolism. However, it is highly detrimental to humans, and high concentrations of Cr can result in anemia, hemolysis, liver, and renal failure (Clarkson, 1991). On the other hand, deficiency of $Cr^{+3}$ causes disturbance in blood glucose, especially in diabetic patients (Sun *et al.*, 2015).

For many years, uptake of some elements, such as Fe and Zn, were not considered as a threat to human health. In contrast, deficiency of these essential elements was the primary concern in developing countries (Akbari *et al.*, 2017). Anemia (WHO, 2001) and death under the age of 5 years due to infection as a result of Fe and Zn deficiency are still major global health problems that are related to low bioavailability of these essential elements and less intake in diet (Bailey *et al.*, 2015). Like other underdeveloped countries, in Iran, Fe intake is below the recommended levels (Aberournand, 2012). However, studies about metal contamination in different parts of Iran showed that the bioavailability of these essential elements is increasing due to an increase in food contamination (Dadar *et al.*, 2017; Shahsavani *et al.*, 2017; Zafarzadeh *et al.*, 2018). Moreover, unlike Western diet wherein meat is a predominant component, Iranian diet relies heavily on agricultural products like rice, fruits, and vegetables (Hashemi *et al.*, 2017). In spite of these elements being essential for humans, their toxicity and bioavailability in food in a specific concentration are of immense concern to public health. In this context, some assessments and monitoring of heavy metals in agricultural products have been conducted in different parts of Iran (Derakhshan *et al.*, 2016). However, there is no information about the accumulation of essential elements in fruits farmed close to industrial-agricultural sites, such as Markazi province. The previously conducted study reported that soil and irrigation water of Markazi province were excessively polluted with lead (Pb) and mercury (Hg) due to the industrial chemicals and effluents (Ghasemidehkordi *et al.*, 2018b); however, there is no record regarding the levels of essential elements in the fruits, soil, and water of this area. Therefore, an investigation is vital for the production of best-quality fruits for inhabitants. In the previous studies, only one study investigated the level of elements, such as Fe, Cu, Zn, Mn, Cr, calcium (Ca(, potassium (K), magnesium (Mg), phosphorus (P) and selenium (Se), in hen egg-white in the Markazi province (Rezaei *et al.*, 2016). However, no studies have been conducted to determine the level of essential elements in fruits produced in this area.

In this context, this is the first attempt to employ an ICP-OES technique to investigate the concentrations of Fe, Cu, Zn, Mn, and Cr in five of the most popular fruits. The level of these elements in irrigation water and the surrounding soil was measured to calculate the transfer factor (TF) value. Moreover, target hazard quotient (THQ), total target hazard (TTHQ), hazard index (HI), and estimated daily intake (EDI) for different groups of consumers in the study area was assessed.

## Material and Methods

### Study area

Six different sites of the Markazi province, namely, Saveh, Khondab, Khomein, Mahallat, Tafresh, and Delijan were selected considering their proximity to several big industrial complexes in the province, including an oil refinery, a petrochemical company, and an aluminum company for the sampling of fruits, water, and soil (Figure 1). Markazi province is located in the western part of Iran (at a latitude and longitude of 34° 05' 30.26" N and 49° 41' 20.98" E, respectively), with an average height of 1,750 m above sea level and a mean annual precipitation of 278 mm/year (relative humidity of 46%). The mean temperature is 12.8°C, and minimum and maximum annual absolute temperatures were −13 to −35°C and 36 to 49°C, respectively. The population of this area is about 1.43 million.

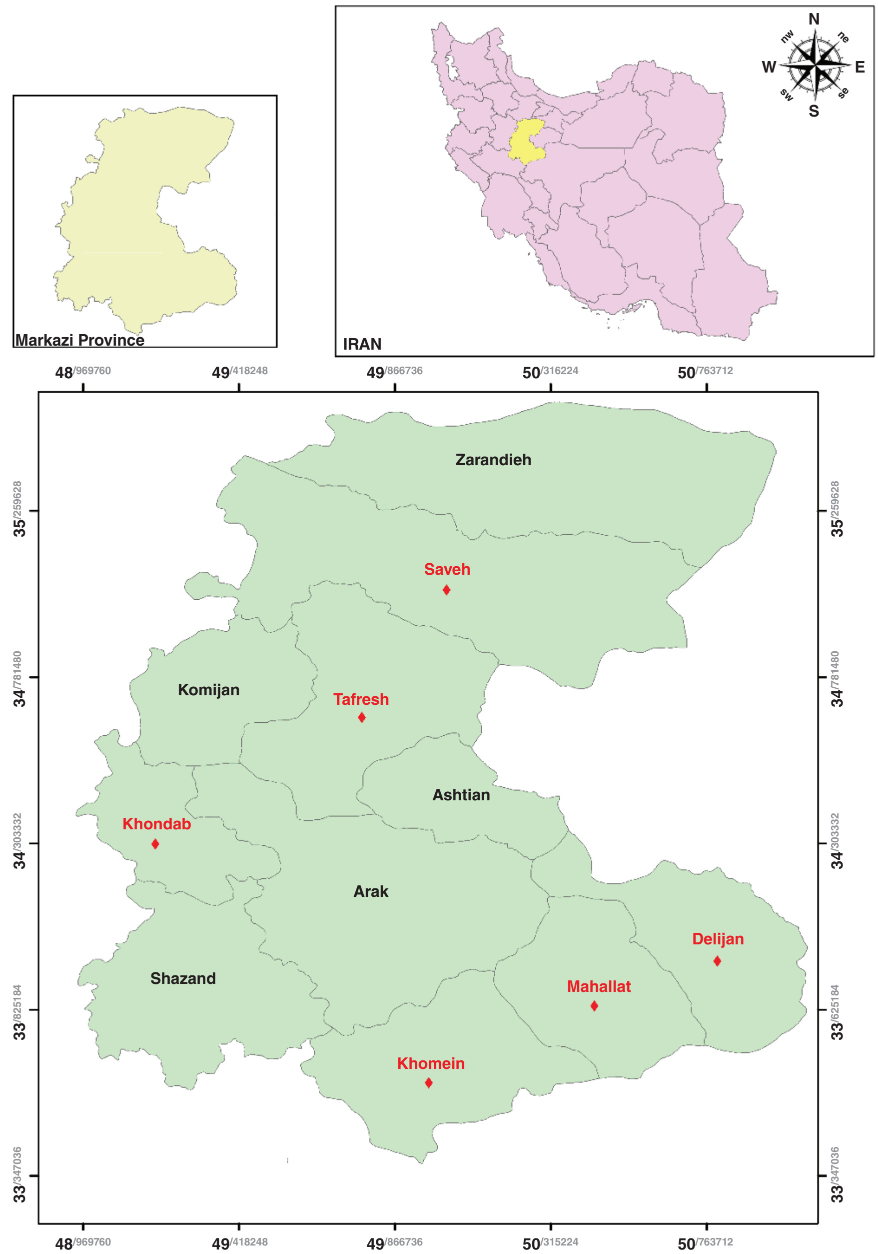


**Figure 1. Map of the sampling localities at Markazi province.**

### Chemical and reagent

All chemicals such as $HNO_3$, $H_2SO_4$, and $HClO_4$ as well as the standards and stock solutions of analytical grade [Fe (Chemical Abstracts Service; CAS) Number 7439-89-6), Mn (CAS Number 7439-96-5), Zn (CAS Number 7440-66-6), Cu (CAS Number 7440-50-8), and Cr (CAS Number 7440-47-3)] were obtained from Merck (Darmstadt, Germany) and were prepared by diluting in ultrapure water.

### Sample collection (fruits, water, and soil)

Five popular fruits species commonly known as peach (*Prunus persica*), apple (*Malus pumila*), grape (*Vitis vinifera L.*), nectarine (*P. persica* var. nucipersica), and golden plum or Mirabelle plum (*P. domestica* subsp. *syriaca*) (triplicate) were collected from selected sites of Markazi. Three samples of each fruit species (1 kg of each sample) were collected. Therefore, 15 samples obtained from the six selected regions resulted in a total of 90 samples (five types of fruits in triplicate from six sampling areas). Also, from each sampling site, 1 kg of soil from around the same trees from which the fruits were plucked was taken (by excavating 1.5 m radial distance from the plant center) and placed into polyethylene bags and preserved in a frozen condition in the laboratory in order to reduce the risk of hydrolysis and oxidation. Samples were taken from 10 to 15 cm depth in the ground while the grass, stones, weeds, and trash were discarded. Water samples (1 L of each sample) was collected in clean glass bottles from irrigation sources in experimental zones.

### Preparation of samples (fruits, water, and soil)

The fruits were collected from the field in polyethylene bags and were transferred to the laboratory as soon as possible to reduce unwanted pollution. Fruit samples were digested by the modified method of Li *et al*. (2019) as follows:

Samples were washed carefully with tap water, and then with ultrapure water; they were chopped to small pieces (only edible parts of the fruit were used). All samples were oven-dried at 70°C for 48 h. Then, they were crushed to the small fragments and stored in dark polyethylene bottles for the next step. Fruit samples (1 g of dried fruits) were acid digested with the aid of a high-pressure microwave-assisted apparatus (MARS 5, CEM Corporation; a maximum power of 1400 W, a power of 100%, 20 mi ramp adjusted, a pressure of 180 psi, 210°C, and a hold time of 10 min) after incorporation of 15 mL of the three acid mixtures to the test tubes, namely, $HNO_3$ (70%), $H_2SO_4$ (65%), and $HClO_4$ (70%), in 5:1:1 ratio. Ultrapure water was added to the remaining solution until it reached 25 mL. Finally, it was subjected to further analysis by an ICP-OES instrument (Shakya and Khwaounjoo, 2013). All calculations were based on fresh weight and the edible portion of fruits.

Soil samples were dried in an oven (70°C for 24 h) before treatment. Soil and water was prepared based on the previously conducted methods (Ghasemidehkordi *et al.*, 2018b; Shakya and Khwaounjoo, 2013).

### ICP-OES analysis

The fruit, soil, and water samples were analyzed for Fe, Cu, Zn, Mn, and Cr by ICP-OES (EOP, Spectroacros, Germany. Model Varian Vista-MPX). The ICP-OES instrument was used according to previously recommended conditions (Ghasemidehkordi *et al.*, 2018a; Shakya and Khwaounjoo, 2013). Equipped with an ultrasonic nebulizer and an autosampler, argon (carrier gas with purity 99.999%), the flow rate for modified lichte nebulizer was 0.7 L/min and for the coolant was 13 L/min. The speed of the four-channel peristaltic pump in pre-flush condition: 60 rpm for 45 S and analysis: 30 rpm, power level: 1400 KW.

### Quality assurance

Individual stock standard solutions (10 μg/mL) were plotted based on the previously conducted studies) 0.1, 0.5, 2.5, 10, 100, 200, 300, and 500 μL of mixed standard stock solution to 10 g of blank samples (Ghasemidehkordi *et al.*, 2018a, 2018b; Rezaei *et al.*, 2017). The linearity of the method was assessed using the calibration curve, and it was plotted for each element in the standard solution and food matrix according to the correlation coefficient ($R^2$) through linear regression analysis.

The sensitivity of the used methods was evaluated using the limit of detection (LOD) (signal-to-noise – S/N ratios of 1/3) and limit of quantification (LOQ) (S/N 1/10).

Spiked fruits, soil, and blank water samples at concentrations of 15, 25, 75, 150, 250, 500, and 750 μg/mL were in triplicates, and the recoveries were measured according to previous investigations (Ghasemidehkordi *et al.*, 2018b).

### Transfer factor

Transmission of elements from soil to plant tissues is defined as TF. It is calculated as a ratio of concentration of elements in plant tissues to the concentration of the same elements in the surrounding soil (Lato *et al.*, 2012). TF > 1 indicates the plant's high absorption of elements from the soil.

### Probabilistic health risk assessment

*Estimated daily intake*

The calculation of estimated daily intake (EDI) (µg/kg-d) was done according to the following equation (Adel *et al.*, 2016).

$$EDI = \frac{C \times IR \times EF \times ED \times CF}{BW \times ATn} \quad \textbf{Equation (1)}$$

C is a concentration of individual essential elements; IR, ingestion rate; EF, exposure frequency; ED, exposure duration; BW, body weight; ATn, average lifespan time, and CF, convert factor. Values of all parameters in equation (1) are presented in Table 1.

*Noncarcinogenic risk assessment*

Noncarcinogenic risk of the elements in fruit samples was measured via THQ based on the following equation (Shahsavani *et al.*, 2017; Zafarzadeh *et al.*, 2018).

$$THQ_i = \frac{EDI}{RfD} \quad \textbf{Equation (2)}$$

where EDI (µg/kg-d) is estimated daily intake and RfD is the reference dose of the essential elements due to the oral pathway. Oral RfD for Fe, Cu, Zn, Mn, $Cr^{+6}$ is 700, 40, 300, 140, and 3 µg/kg-d, respectively (EPA, 2017).

Likewise, the TTHQ was calculated through the following equation (Shi *et al.*, 2011; USEPA, 2015).

$$TTHQ = \sum_{i=1}^{n} THQi \quad \textbf{Equation (3)}$$

where TTHQ is the sum of THQ of each essential element in fruits when THQ and/or TTHQ > 1, the health risk is considerable; if THQ and/or TTHQ ≤ 1, there is no likelihood of a health risk (Dadar *et al.*, 2017).

The quota of essential elements in TTHQ was determined through the current equation (Shi *et al.*, 2011; USEPA, 2015):

$$Q = \frac{THQe}{TTHQ} \times 100 \quad \textbf{Equation (4)}$$

where Q is a quota of essential elements (%), THQ is THQ of any element, and TTHQ is the total THQ.

*Monte Carlo simulation model*

Uncertainties can be undertaken in risk assessment (Chen *et al.*, 2012). High uncertainty can expected while a single-point value like a concentration in the health risk assessment was used. Therefore, Monte Carlo simulation (MCS) can be used as a model to decrease the uncertainties (Ru *et al.*, 2013). Probabilistic risk assessment was done using Crystal Ball software (version 11.1.2.4, Oracle, Inc., USA). Ninety five percent of THQ was a benchmark for endangered population. The number of 10,000 was also selected as repetitions in the model (Qu *et al.*, 2012).

*Statistical analysis*

The mean value, standard deviation (SD), and one-way analysis of variance (ANOVA) test were conducted to determine the concentrations of essential elements in samples. $P < 0.05$ was considered statistically significant. These analyses were performed using the SPSS v.22 (Chicago, IL, USA).

## Results and Discussion

### Quality assurance

All essential elements presented good linearity. The correlation factors for the essential elements were between 0.9974 and 0.9998.

**Table 1. Included parameters to health risk assessment.**

| Parameter | Definition | Unit | Value | References |
|---|---|---|---|---|
| EDI | Estimated daily intake | mg/kg-d | | |
| C | Concentration | µg/kg | | |
| IR | Ingestion rate | g/d | Children = 12<br>Adults = 30 | (Fathabad *et al.*, 2018) |
| EF | Exposure frequency | d/Year | 350 | |
| ED | Exposure duration | Years | Children = 6<br>Adults = 30 | (USEPA, 2015) |
| BW | Body weight | Kg | Children = 15<br>Adults = 70 | |
| Atn | Average lifespan time for noncarcinogenic risk | days | Children = 2190<br>Adults = 10,950 | (USEPA, 2015) |
| CF | Convert factor µg to mg | | $10^{-3}$ | |

The LOQs for Fe, Cu, Zn, Mn, and Cr were calculated as 0.53, 0.99, 0.89, 0.23, and 0.33 μg/kg, respectively. The LODs of these essential elements were 0.16, 0.30, 0.27, 0.07, and 0.10 μg/kg, respectively (Table 2).

The recoveries of the investigated essential elements at these six spiking levels were presented in Table 2. Repeatability of the essential elements were relative standard deviation (RSD) < 20% with n = 3 at each spiking level.

### The concentrations of essential elements in fruits

The levels of essential elements in different fruits in studied area were demonstrated in Table 3. The golden plum was a valuable source of Cr, Fe, Mn, and Zn with 6.16 ± 2.81, 168.32 ± 101.96, 19.51 ± 9.98, and 12.20 ± 7.63 μg/kg, respectively. The highest concentrations of Cu were observed in grape samples with a mean of 27.91 ± 14.18 μg/kg.

A significant difference in the content of the elements between fruit species ($P < 0.05$) was noted (Table 3). This could be attributed to many factors, such as different uptake levels and accumulation capacities among fruit species, different pH, organic matter contents, different soil characteristics, the amount of fertilizer used, and irrigation with contaminated wastewater (Duran *et al.*, 2008). In a study conducted in Turkey, the levels of Fe, Cr, and Mn in golden plum were reported as 41,320 ± 3800, 6170 ± 600, and 6470 ± 570 μg/kg, respectively. However, in agreement with the result of the current study, they reported that the highest amount of Cu (4529 ± 370 μg/kg) and Cr (6170 ± 600 μg/kg) were correlated with grape and golden plum, respectively (Duran *et al.*, 2008). The mean concentrations of 5 ± 0.00 μg/kg for Cu and 65 ± 40 μg/kg for Zn in apple and 15 ± 20 μg/kg for Cu and 63 ± 90 μg/kg for Zn in grape were reported by a study conducted in the northwest of Iran (Ehsani *et al.*, 2015). Besides, based on the Institute of Medicine (IoM), in the United States, the tolerable upper intake level (UL) for adults was determined to be 45,000, 10,000, 40,000, and 11,000 μg/day of Fe, Cu, Zn, Mn, respectively (IOM, 2001). The concentrations of the elements in the current investigation were lower or within the safe range.

According to the level of elements in different places and fruits, we can conclude that the highest levels of Cr, Fe, Mn, Zn, and Cu were observed in Khondab plum, while Cu concentrations were higher in Tafresh. The lowest levels of Fe and Mn were found in Mahallat grape. The lowest levels of Zn and Cu were observed in Tafresh and Khondab nectarine, respectively (Table 3). These various concentrations of elements in fruits from different regions can be attributed to the type of soil, water, air, fertilizer, and pesticides. As the results show, the concentrations of several elements, for example, Cu and Mg in Saveh, are very high compared to the other sampling areas, most likely due to the composition and type of fertilizer used in that area.

Recently, in Iran, the source of contamination of elements is not only industrial pollution and the excessive use of

**Table 2. Average recoveries (%), relative standard deviations (%), LOD, and LOQ (μg/kg) obtained by ICP-OES analysis at six spiking levels (n = 3) in fruit, soil, and water samples.**

| Metal | Samples | Recovery (n = 18) | Range of RSD (n = 3) | LOD | LOQ |
|---|---|---|---|---|---|
| **Cr** | Fruits | 113.70 ± 7.57 (100.46–117.79) | 5.11–18.91 | 0.10 | 0.33 |
| | Soil | 96.10 ± 10.01 (86.55–115.28) | 5.70–15.82 | | |
| | Water | 110.06 ± 4.93 (105.45–114.84) | 7.34–19.75 | | |
| **Cu** | Fruits | 100.34 ± 8.08 (89.68–110.54) | 5.70–17.40 | 0.30 | 0.99 |
| | Soil | 89.68 ± 16.43 (86.07–115.33) | 2.80–19.00 | | |
| | Water | 110.92 ± 6.99 (100.51–119.91) | 3.70–14.70 | | |
| **Fe** | Fruits | 111.56 ± 7.83 (101.89–120.94) | 4.92–19.30 | 0.16 | 0.53 |
| | Soil | 95.34 ± 7.33 (84.13–103.75) | 4.20–18.23 | | |
| | Water | 109.13 ± 8.13 (99.39–118.64) | 3.30–17.80 | | |
| **Mn** | Fruits | 101.48 ± 6.26 (90.30–109.28) | 6.20–19.30 | 0.07 | 0.23 |
| | Soil | 88.48 ± 15.12 (74.77–108.76) | 5.85–17.25 | | |
| | Water | 109.85 ± 5.82 (101.71–118.54) | 1.72–14.93 | | |
| **Zn** | Fruits | 110.70 ± 8.56 (96.71–119.66) | 2.80–11.10 | 0.27 | 0.89 |
| | Soil | 97.25 ± 12.16 (86.08–113.86) | 5.90–16.60 | | |
| | Water | 108.30 ± 11.84 (92.56–119.84) | 3.80–14.90 | | |

**Table 3. The mean level and standard deviation of different elements in different fruits of the studied area (μg/kg. dw).**

| Location | Plum | | | | | Apple | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Cr | Cu | Fe | Mn | Zn | Cr | Cu | Fe | Mn | Zn |
| **Tafresh** | 8.08 ± 1.72 | 18.09 ± 2.39 | 276.28 ± 10.03 | 29.33 ± 0.02 | 15.00 ± 0.76 | 1.21 ± 0.03 | 4.30 ± 2.74 | 25.96 ± 7.23 | 2.68 ± 1.01 | 3.50 ± 0.20 |
| **Delijan** | < LOD | 17.63 ± 2.17 | 215.31 ± 12.16 | 28.02 ± 0.47 | 3.41 ± 0.13 | < LOD | 4.33 ± 2.01 | 27.20 ± 6.95 | 4.60 ± 1.20 | 4.21 ± 0.52 |
| **Saveh** | < LOD | 17.52 ± 1.18 | 60.36 ± 7.23 | 9.38 ± 0.23 | 7.14 ± 0.04 | 1.44 ± 0.11 | 6.83 ± 2.20 | 35.89 ± 9.69 | 5.61 ± 1.12 | 5.89 ± 0.13 |
| **Khomein** | 7.08 ± 0.01 | 33.54 ± 2.74 | 100.60 ± 11.63 | 15.79 ± 1.01 | 8.52 ± 0.07 | < LOD | 11.55 ± 2.56 | 62.04 ± 11.63 | 4.21 ± 1.30 | 9.08 ± 0.61 |
| **Mahallat** | 1.68 ± 0.12 | 17.63 ± 2.12 | 60.36 ± 7.23 | 9.35 ± 0.25 | 11.87 ± 0.79 | 1.21 ± 0.01 | 35.95 ± 0.66 | 180.81 ± 12.16 | 20.52 ± 0.47 | 16.01 ± 0.31 |
| **Khondab** | 8.12 ± 0.21 | 33.62 ± 2.54 | 279.28 ± 11.63 | 29.33 ± 3.47 | 25.16 ± 1.33 | < LOD | 3.13 ± 2.17 | 25.86 ± 7.17 | 1.88 ± 0.23 | 17.60 ± 0.87 |
| **Total** | 6.16 ± 2.81[a] | 23.40 ± 11.84[a] | 168.32 ± 101.96[a] | 19.51 ± 9.98[a] | 12.20 ± 7.63[a] | 1.31 ± 0.11[b] | 11.67 ± 11.58[a] | 60.90 ± 59.73[b] | 6.93 ± 6.48[a] | 9.76 ± 5.83[b] |
| **Location** | **Grape** | | | | | **Peach** | | | | |
| | Cr | Cu | Fe | Mn | Zn | Cr | Cu | Fe | Mn | Zn |
| **Tafresh** | < LOD | 9.83 ± 0.66 | 27.20 ± 0.85 | 4.60 ± 0.74 | 12.50 ± 0.50 | < LOD | 11.55 ± 2.20 | 68.55 ± 6.65 | 6.61 ± 0.73 | 16.4 ± 0.10 |
| **Delijan** | 1.18 ± 0.01 | 20.01 ± 0.58 | 29.07 ± 1.48 | 12.70 ± 0.85 | 3.88 ± 0.06 | 1.92 ± 0.01 | 28.60 ± 3.01 | 254.32 ± 3.82 | 14.56 ± 0.61 | 3.81 ± 0.13 |
| **Saveh** | 1.51 ± 0.02 | 56.04 ± 1.24 | 229.47 ± 2.29 | 27.73 ± 1.01 | 7.21 ± 0.22 | < LOD | 11.75 ± 2.75 | 94.04 ± 11.63 | 6.04 ± 0.55 | 6.45 ± 0.25 |
| **Khomein** | 1.28 ± 0.10 | 35.95 ± 0.10 | 178.81 ± 1.79 | 21.52 ± 1.47 | 10.85 ± 0.40 | 1.21 ± 0.20 | 9.05 ± 2.08 | 286.95 ± 5.51 | 10.09 ± 0.51 | 8.03 ± 0.07 |
| **Mahallat** | 1.17 ± 0.02 | 5.19 ± 0.55 | 17.86 ± 1.21 | 1.88 ± 0.18 | 6.68 ± 0.10 | 7.08 ± 0.02 | 18.51 ± 3.03 | 88.58 ± 11.63 | 9.28 ± 0.61 | 13.92 ± 0.39 |
| **Khondab** | < LOD | 35.79 ± 1.10 | 148.01 ± 3.91 | 17.22 ± 0.47 | 23.55 ± 0.49 | 1.18 ± 0.10 | 8.12 ± 2.74 | 142.30 ± 7.65 | 8.14 ± 0.15 | 17.47 ± 0.12 |
| **Total** | 1.28 ± 0.16[b] | 27.91 ± 14.18[ab] | 102.38 ± 76.73[b] | 14.54 ± 8.26[a] | 12.65 ± 6.69[ac] | 2.86 ± 2.57[c] | 15.51 ± 7.78[ac] | 155.42 ± 72.06[b] | 9.68 ± 2.44[b] | 11.01 ± 5.32[ad] |
| **Location** | **Nectarine** | | | | | | | | | |
| | Cr | Cu | Fe | Mn | Zn | | | | | |
| **Tafresh** | 1.92 ± 0.01 | 27.95 ± 1.12 | 62.04 ± 11.63 | 5.21 ± 1.01 | 3.41 ± 0.01 | | | | | |
| **Delijan** | 1.21 ± 0.06 | 3.80 ± 0.55 | 25.86 ± 7.23 | 1.88 ± 0.23 | 3.65 ± 0.02 | | | | | |
| **Saveh** | 1.22 ± 0.02 | 27.95 ± 1.49 | 110.81 ± 12.16 | 10.52 ± 0.47 | 6.74 ± 0.011 | | | | | |
| **Khomein** | 1.18 ± 0.10 | 8.53 ± 0.66 | 55.24 ± 11.61 | 6.41 ± 1.12 | 8.68 ± 0.23 | | | | | |
| **Mahallat** | 1.17 ± 0.04 | 8.82 ± 0.66 | 117.69 ± 11.23 | 8.47 ± 1.02 | 14.34 ± 0.36 | | | | | |
| **Khondab** | < LOD | 10.92 ± 0.62 | 36.69 ± 11.13 | 4.82 ± 1.20 | 19.52 ± 0.55 | | | | | |
| **Total** | 1.35 ± 0.30[d] | 13.14 ± 3.81[d] | 65.40 ± 58.36[b] | 6.17 ± 2.07[b] | 6.21 ± 9.57[acd] | | | | | |

*Different letters in the same column indicate significant differences ($P < 0.05$).
Cr, Chromium; Cu, Copper; Fe, Iron; Mn, Manganese; Zn, Zinc; Limit of detection, LOD; Limit of quantification, LOQ.

chemical pesticides but also the overuse of manure and other chemical fertilizers in the soil (Hatamikiya *et al.*, 2018). Furthermore, it has been demonstrated that most plants need an adequate amount of elements for healthy growth, and usually in Iran artificial or combined inorganic fertilizers are used to fortify the soil and the plant to provide the necessary essential elements such as Cu (Maleki and Zarasvand, 2008). Therefore, element contamination may not be only due to industrial contamination. Therefore, attention should be paid to agricultural products even if they are not grown near an industrial area. Moreover, different plant species have different capacities for accumulation (Mirecki *et al.*, 2015). Therefore, another suggestion is to apply optimal programs for cultivating alternative plants with low accumulation capacity near the industrial area. Similarly, a study in India on vegetables showed that Fe is the most abundant element in fruits, which is also in agreement with the reported results (Kooner *et al.*, 2014).

In the present study, the mean levels of Cu were 18.34 ± 12.16 μg/kg, with the highest levels reported in grape and the lowest in apple. These reports are consistent with the reports of Duran *et al.* (2008), where mean concentrations of Cu ranged from 1.68 to 4.52 μg/kg. Their study showed that the highest level was observed in black grape while the lowest level was observed in white mulberry (Duran *et al.*, 2008). According to Pipoyan *et al.* (2019), the farmlands' tailing repositories were the reason for the high Cu concentration in fruits and vegetables (Pipoyan *et al.*, 2019).

### The concentrations in soil and water samples

The mean concentrations of Cr, Cu, Fe, Mn, and Zn in the soil were 221.90 ± 74.30, 772.50 ± 204.70, 383306.20 ± 90254.20, 13415.00 ± 3557.10, and 1787.60 ± 441.40 μg/kg, respectively (Table 4). Maximum permissible concentration (MPA) of Cu, Zn, and Cr are 30, 200, and 100 mg/kg, respectively (Sudhakaran *et al.*, 2018). Soil samples of the Khomein contained the highest levels of Cr and Fe (353.46 ± 8.62 and 495074.00 ± 251.63 μg/kg, respectively) while soil samples from Tafresh and Delijan contained the lowest level of these elements (164.69 ± 8.12 and 233,870 ± 252 μg/kg, respectively). The highest levels of Cu, Mn, and Zn in soil samples were observed in Khondab, Tafresh, and Delijan, respectively (974.42 ± 11.23, 16993.66 ± 84.27 and 2470.11 ± 2.01 μg/kg). At the same time, soil samples from Saveh contained the lowest level of these elements (489.19 ± 12.01, 9042.14 ± 82.32, and 1024.53 ± 1.73 μg/kg, respectively). This dispersion could be due to the type of soil in different geographic regions and the different agricultural processes in the studied areas. The use of soil fertilizers is a significant factor because the use of the same type of fertilizer by all farmers in one area ultimately leads to homogeneity of certain elements (e.g., Fe, Mn, and Zn in water samples of Khomein) in the soils of that area.

In a similar investigation regarding soils collected from different farms in China, the concentrations of Cr, Cu, and Zn were 58,870, 31,710, and 117,720 μg/kg, respectively (Wei and Yang, 2010). Also, Mico *et al.* (2006) reported that the concentrations of Fe, Mn, Zn, Cr, and Cu in Spanish agricultural soils were 13,608,000, 295,000, 53,000, 27,000, and 23,000 μg/kg, respectively (Micó *et al.*, 2006).

Ennaji *et al.* (2020) reported that the mean concentrations of Cd, Cr, Cu, and Zn in the agricultural soil of the northeast area of Tadla plain, Morocco, were 32.72, 138.10, and 162.11 mg/kg, respectively. Also, they stated that these values are higher than the acceptable thresholds of the World Health Organization (WHO) and the Food and Agriculture Organization (FAO) (Ennaji *et al.*, 2020). Fan *et al.* (2020) showed that the concentrations of Cr and Zn in all samples collected from an agriculturally dominated region in eastern China were lower than the risk-screening values (Fan *et al.*, 2020). Varol *et al.* (2020) studied the content of trace elements in soils of Harran Plain, Turkey, and concluded that Cu and Cr's carcinogenic risk values were within the acceptable risk range (Varol *et al.*, 2020).

**Table 4. The minimum, maximum, and mean ± SD concentration of the studied elements in the experimented soil and water (μg/kg or liter).**

| | | Cr | Cu | Fe | Mn | Zn |
|---|---|---|---|---|---|---|
| **Water** | Min | < LOD | < LOD | 54.80 | 363.90 | 68.00 |
| | Max | < LOD | < LOD | 2982.90 | 620.00 | 641.90 |
| | Mean ± SD | < LOD | < LOD | 1316 ± 1108 | 483.80 ± 112.90 | 327.90 ± 182.11 |
| **Soil** | Min | 156.30 | 479.10 | 233618.40 | 8949.70 | 1023.20 |
| | Max | 362.30 | 986.50 | 495325.60 | 17066.10 | 2472.10 |
| | **Mean ± SD** | **221.90 ± 74.31** | **772.50 ± 204.72** | **383306.20 ± 90254.22** | **13415.00 ± 3557.11** | **1787.60 ± 441.42** |

Limit of detection, LOD; Cr, Chromium ; Cu, Copper ; Fe, Iron ; Mn, Manganese ; Zn, Zinc; Min, minimum; Max, maximum.

**Table 5. The total mean value of TF and RfD of elements (μg/kg-d).**

| | Cr | Cu | Fe | Mn | Zn |
|---|---|---|---|---|---|
| **TF** | 0.0120 ± 0.0090 | 0.0220 ± 0.0090 | 0.0003 ± 0.0001 | 0.0010 ± 0.0002 | 0.009 ± 0.002 |
| **RfD*** | 3 | 40 | 700 | 140 | 300 |

*Reference dose.
TF, transfer factor; Cr, Chromium ; Cu, Copper ; Fe, Iron ; Mn, Manganese ; Zn, Zinc.

The concentrations of these elements are higher than the results of the present study. Elements like Fe and Mn can be influenced by the available microorganisms in the soil activity to extend their bioavailability and facilitate their uptake through the root of the plant (Wilberforce, 2016). Metal solubility in the soil is another factor that differs between metals (Xu *et al.*, 2013). Besides, the composition of the soil (clay, organic material, and pH) alters Zn bioavailability, which causes a wide range of Zn concentrations in different soils (Noulas *et al.*, 2018).

Regarding water samples, the concentrations of Cr, Cu, Fe, Mn, and Zn were in the ranges of < LOD, < LOD, 1316 ± 1108, 483.80 ± 112.90, and 327.90 ± 182.10 μg/l, respectively (Table 4). The rank order of average concentrations of the elements in the investigated soil and water samples was Fe > Mn > Zn > Cu > Cr. The highest Fe, Mn, and Zn concentrations in the water were observed in Khomein, while the lowest concentrations of these elements were found in Saveh, Mahallat, and Saveh, respectively.

## TF of the essential elements in fruits

The TF calculated of Cr, Cu, Fe, Mn, and Zn in five fruits species from the surrounded soils were 0.01 ± 0.01, 0.02 ± 0.01, 0.0003 ± 0.0001, 0.0010 ± 0.0002 and 0.009 ± 0.002, respectively (Table 5). Metals could have different compositions in the soil, such as carbonate, oxide, or organic, which could affect their uptake by plants (Fijałkowski *et al.*, 2012). There is no correlation between the amount of elements in the water and soil of one area and the extent of elements in the fruits of the same area. The high or low levels of water and soil elements did not significantly affect their concentrations in cultivated fruits, which is also shown by the TF result.

According to TF index description, TF < 1 means lower absorption of elements from the soil (Ali *et al.*, 2019). The reported TF results indicate that fruits cannot accumulate high levels of these elements from the soil. However, it has been reported that even if the level of elements such as Cr in the soil is in the WHO standard range, some plants uptake more concentrations, and the accumulation level is at a dangerous level (Maleki *et al.*, 2014). According to the finding of a previous investigation, when TF in samples is higher than 0.5, the plant will have a higher potency of metal contamination in the environment (Khan *et al.*, 2009; Mirecki *et al.*, 2015). Heidari *et al.* (2014) stated that fruit trees (involving apple trees) near industrial sites accumulate a dangerous amount of elements like Cr. Moreover, considering identical soil conditions, the accumulation of the elements varies in different parts of the plants. Also, it differs with regard to the type of plant species, and it has been shown that the order of accumulation in edible plants is: leaf vegetables > fruit vegetables > root vegetables > grains (Mirecki *et al.*, 2015). The current study focused on fruit tissues only; therefore, attention should be paid to the other parts of plants (if they are edible or are used during the food processing) or other types of crops or vegetables, especially their leafy part is cultivated in a polluted area.

## Risk assessment

### *Noncarcinogenic and carcinogenic risks*

THQ (percentile 95%) in adults due to intake of Fe, Cu, Zn, Mn, and Cr through consumption of fruits were 1.24E-3, 1.85E-3, 4.80E-8, 7.69E-8, and 1.21E-5, respectively (Figure 2 A–E). Also THQ (percentile 95%) in children for the same elements was 2.23E-3, 1.45E-7, 2.20E-5, 3.37E-5, and 9.02E-7 respectively (Figure 3 A–E). The rank order of elements based on their THQ in adults and children was Cr > Cu > Fe > Mn > Zn. THQ of Cr was higher than other essential elements because of its lower RfD (EPA, 2012). THQ in children was 1.87 times higher than adults because they have lower body weight (Abtahi *et al.*, 2017; Adel *et al.*, 2016; Fakhri *et al.*, 2017).

The rank order of elements based on TTHQ was Cr (44.34%) > Cu (34.07) > Fe (11.77%) > Mn (6.03%)> Zn (3.79%) (Figure 4). TTHQ (Percentile 95%) due to all elements (Cr, Cu, Fe, Mn, and Zn) in adults and children was 5.524E-07 and 1.0334E-06, respectively (Figure 4), which was lower than 1. THQ and TTHQ in both adults and children were <1 because of the low ingestion rate of fruits and the low concentrations of essential elements

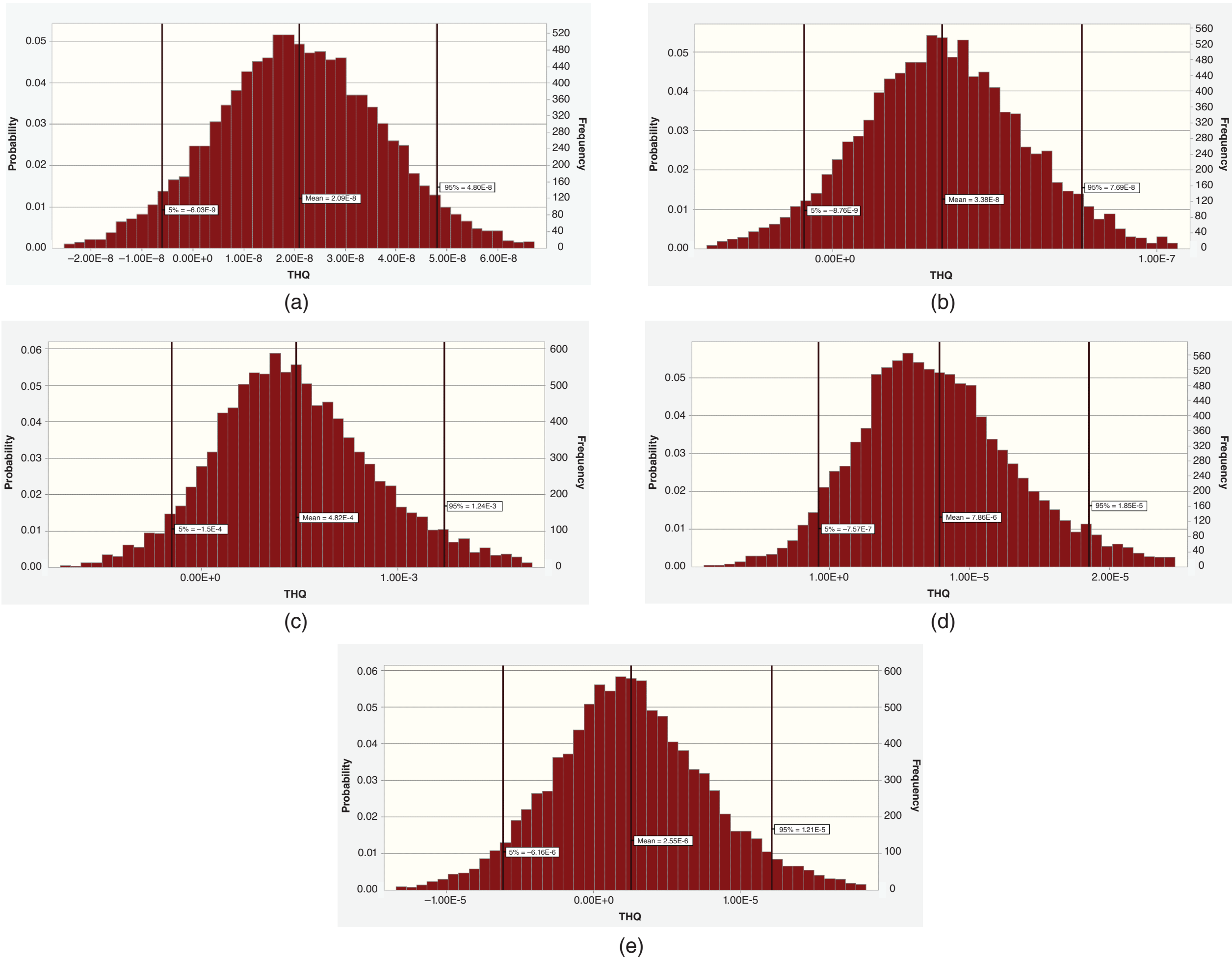


**Figure 2. Target hazard quotient (THQ) in adults due to ingestion fruits content of Zn (A), B (Mn), C (Fe), D (Cu), and E (Cr) via fruits consumption.**

(Abtahi *et al.*, 2017; Adel *et al.*, 2016; Fakhri *et al.*, 2017; Statista, 2013). Therefore, populations are not at a considerable noncarcinogenic risk of essential elements in fruits.

In Pipoyan *et al.* 2019 study, the THQ for the Mo level in cabbage exceeded 1, with 1.65 for males and 1.6 for females, indicating a health risk in consuming cabbage. However, for other fruits and veggies, THQ was < 1, but they could substantially contribute to TTHQ (Pipoyan *et al.*, 2019). Abdelkareem *et al.* (2018) reported that the levels of Zn, Cr, Cu, Fe, and Mn in different fruits in Saudi Arabia were ~ 2,850, 1, 150, 100, and 10 µg/kg, respectively, which were lower than LOD and safe for consumers in terms of the amount of these elements (Abdelkareem *et al.*, 2018). Qureshi *et al.* 2016 reported high levels of Cu, Cr, and Zn in some vegetables in the United Arab Emirates; however, it was lower than the safety standards of the WHO and the European Union (Qureshi *et al.*, 2016).

The findings of the present study demonstrate that the fruit samples used by local people in Markazi province are safe and without any health risk to consumers.

## Nutritional assessment

Grembecka *et al.* (2013) investigated micro and macro elements among different fruits. Based in their findings, Fe has the highest concentration (156 µg/kg in grapefruit), followed by Mn and Zn, (Grembecka and Szefer, 2013). It was in sync with the finding of our study. Basha *et al.* (2014) studied the level of some elements in fruits and vegetables in India. The range of Mn, Fe, Ni, Cu, and Zn was reported as 300–8,100; 6,500–126,300; 100–4,100; 300–3,200; and 100–19,700 µg/kg, respectively, and the trend of the measured essential elements was reported as Fe > Al > Zn > Mn > Cr > Cu > Pb > Ni > Co > V > Cd > Be > U, which is similar to this study. They also reported

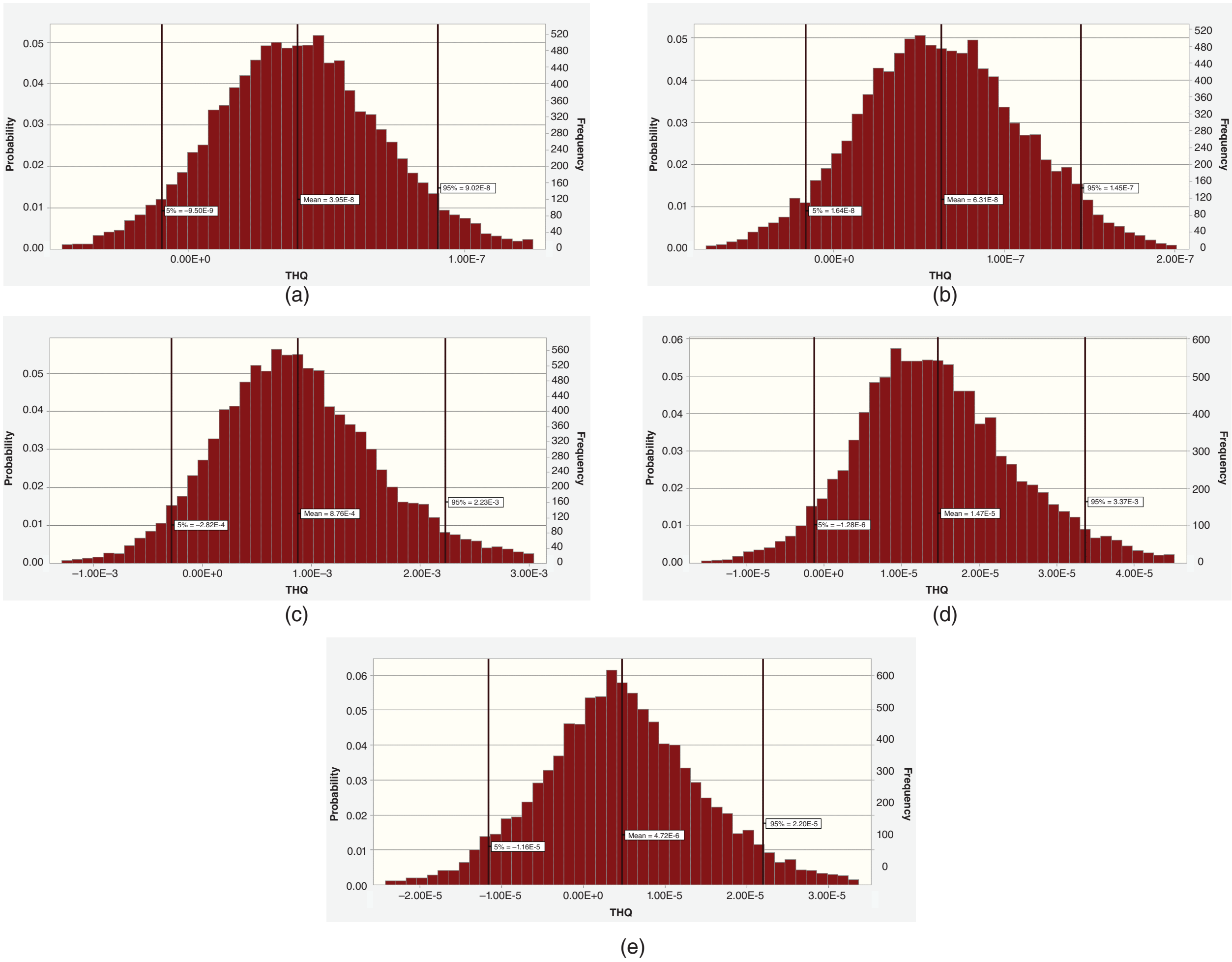


**Figure 3. Target hazard quotient (THQ) in children due to ingestion fruits content of Zn (A), B (Mn), C (Fe), D (Cu), and E (Cr) via fruits consumption.**

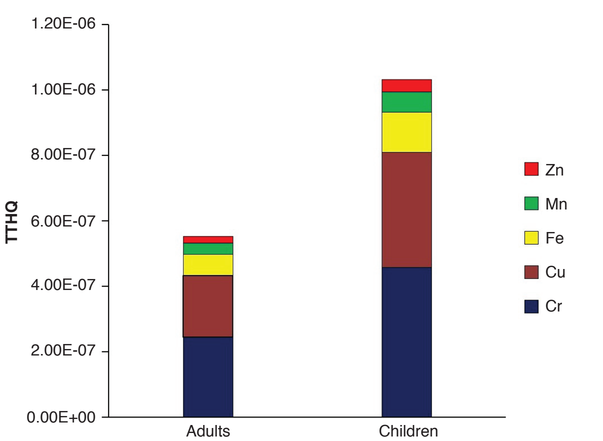


**Figure 4. Total target hazard quotient (TTHQ) in adults and children due to ingestion fruits content of Zn, Mn, Fe, Cu, and Cr.**

that the daily intake Zn, Fe, Mn, and Cu was 600, 3,500, 200, and 100 μg/day, respectively (Basha *et al.*, 2014).

The findings showed that the golden plum is a valuable source of Fe, Mn, and Cr. In this regard, based on the report of Duran *et al.* (2008), the highest concentration of Fe was detected in the apricot with 64.10 μg/kg. They also marked the golden plum as a rich source of Fe (Duran *et al.*, 2008). Also, Sattar *et al.* (1989) demonstrated that the Fe concentration in dried fruits of Pakistan was in the range 19–45 μg/kg dry weight (Sattar *et al.*, 1989), while according to Zahoor *et al.* (2003), the content of this element in fruits of Pakistan was 3,890–40,700 μg/kg wet weight (Zahoor *et al.*, 2003).

## Conclusions

Elements like Fe, Cu, Zn, and Mn quickly enter into food commodities from various sources of the ecosystem.

While they are essential for humans health, in a exceed concentration can resulted in some adverse effects. In this study, concentrations of Fe, Zn, Cu, Mn, and Cr (μg/kg FW) in five highly consumed fruits, namely, peach, apple, grape, nectarine, and golden plum, were determined. According to the results, the highest concentrations of Fe, Mn, and Cr were found in golden plum and that of Cu and Zn were found in the grape, which showed that the golden plum has a high ability to accumulate essential elements and is considered a rich source of elements among fruits. The concentrations of the studied elements were lower than the standards, which mean that the consumption of fruits is safe in terms of the amounts of these elements. The probabilistic health risk revealed that adults and children are not at noncarcinogenic risk (95% THQ and TTHQ < 1). Regarding the ability of elements to accumulate among plant or TF, it could be stated that fruits have a low ability to uptake and accumulate the toxic level of elements in their tissues. The present study demonstrates that these fruits are a valuable diary resource of essential elements. Among them, golden plum and grape may provide a significant daily intake dose of these elements.

## Conflict of interest

The authors declare that they have no conflict of interest.

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