Trace Metal Determination in Herbal Plants by Acid Digestion from Jeddah Market in Saudi Arabia

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Abstract
The world is facing a serious issue for plants contaminated by trace metals. Therefore, it requires consideration due to its danger for both humans and animal. Herbs are extensively used worldwide for their seasoning and therapeutic properties. This study aimed to estimate the level of trace metals in selected customary herbs consumed in Saudi Arabia. The 5 samples of herbs were purchased from a local market in Jeddah City. Acid digestion was applied to the plant leaves and trace metals concentration were determined using Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES). Metals were observed to be available in varied concentrations in the herb plant samples. The highest metal values, especially in Arugula (ES) 218.3±1.9 mg/kg and 24.4±0.09 mg/kg for Zn and Ni respectively, Cr was under detected limit, Coriander (CS) 148.5±1.8 mg/kg and 17.3±0.07 mg/kg for Fe and Pb respectively, Mint (ME) 28.6±0.26 mg/kg for Cu, while Basil (OC) was recorded below the (WHO) permissible limits 18.9± 0.06 mg/kg and 1.1± 0.003 mg/kg for Zn and Cr respectively, besides all metals were higher than the (WHO) allowed limit in Parsley (PC). The study suggests that most of the examined herbs contained hazardous levels of trace metals that exceeded the World Health Organization (WHO) permissible limits.

Keywords: Herbal plants, Trace metals, Acid digestion, Determination, ICP-OES.

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1. INTRODUCTION

Heavy metals found in a trace amount in plants, which has a biological effect that can be toxic to plants and human being through the food chain. In this report the term "trace metals" will be for these possible phytotoxic elements (Rascio and Navari-Izzo, 2011). The most significant sources of trace metals in the nature are the anthropogenic activities, for example mining, steel, iron or chemical industry, smelting method, traffic, farming as well as domestic activities (Suciu *et al.*, 2008). The plants have ability to absorb and accumulate xenobiotic makes them helpful as markers of environmental contamination (Farago, 1994; Pandolfini *et al*., 1997).

The 14 mineral elements are requiring of the plants for full physiological activity. Depending on the element, these range in concentration from 10,000 mg/kg $\geq$ 0.001 mg/kg (Wheal *et al*., 2011). Every nutrient element is essential within an ideal range, which may result, if exceeded, from changes in many physiological processes occurring at the cellular/ molecular level by disabling enzymes, blocking functional groups of metabolic important molecules, substituting essential elements and disrupting the integrity of the membrane (Rascio and Navari-Izzo, 2011). Herbal plants represent an important class of various traditional medicine systems and, in recent years, they are increasingly used in the primary health care intervention in both developed and developing countries. Herbal medicines are extensively used for the treatment of numerous illnesses. They frequently contain highly effective pharmacological components, including minerals and trace metals (Fabricant and Farnsworth, 2001).

In parallel with the increasing attention of the therapeutic benefits of herbal plants, there is a high concern about the safety and poisonous of natural herbs and formulation given out in the market. There is a widespread misconception that natural herbs and plants are inherently safe. Nevertheless, there has been a large volume of reports on incidences of toxicity and adverse effects linked to the use of herbal plants and their formulations in different parts of the world (AlBraik *et al.*, 2008). The toxicity of herbal plants may be related to contaminants in soil and water such as pesticides, microbes, and chemical toxins also transportation and storage can affect the quality of herbs caused by contaminant air (Ernst, 2002; Saad *et al*., 2006). The toxicity of trace metals on human health and the environment has attracted considerable attention in recent years. Plants are the main link in the transfer of trace metals from the contaminated soil to humans through the food chain. trace metals have low excretion rates through the kidney which could result in damaging effects on humans even at very low concentrations. The essential nutrient metals are Zn, Co, Fe, and Cr, they are important for the physiological and biological functions of the human body. However, an increase in their intake above certain permissible limits can become toxic (Korfali *et al*., 2013). In general, several health problems were linked to excessive uptake of dietary trace metals including a decrease in immunological defenses, cardiac dysfunction, fetal malformation, impaired psychosocial and neurological behavior, gastrointestinal cancer, and many others (Singh *et al.*, 2011; Mahan *et al.,* 2017).

Hence, many techniques were applied for elemental analysis. The most widely recognized strategies utilized nowadays for determining the trace elements in ecological samples include very sensitive spectroscopic methods, for example, inductively coupled plasma-optical emission and mass spectrometry (ICP–OES) and (ICP–MS) and atomic absorption spectroscopy (FAAS, ETAAS). The utilized sample digestion methods are performed by fusion or wet procedure of heating acid mixtures. Various types of heating systems can be utilized, for example, hot plate, sand bath, aluminum blocks and digestion pressure bomb (Altundag and Tuzen, 2011). There is little information available on the safety of traditional herbs and their production seller in the Saudi Arabia market. This study aims for determining the level of trace metals in some commonly consumed herbs were purchased from a local market in Jeddah City to assess their relative safety and potential health risk based on the World Health Organization standard limits (WHO, 2011; Onder *et al.*, 2007).

2. MATERIALS AND METHODS

2.1 Sample collection and preparation

The different 5 herbal Plants 6 samples for each were collected from local market in Jeddah City, Saudi Arabia Table 1. First, the plant samples were washed with tap water for removing all dust and impurities until it become cleaned as the last wash was by distilled water. The second step the samples was drying at room temperature for few days. Finally, the dried plants were grinding using a grinder and stored in plastic bags.

Table 1. Local and botanical name of the herbs and their code

Local name	Botanical name	Code	Parts analyzed
Mint	Mentha	ME	Leaves
Basil	Ocimum	OC	Leaves
Arugula	Eruca Sativa	ES	Leaves
Coriander	Coriandrum Sativum	CS	Leaves
Parsley	Petroselinum Crispum	PC	Leaves

2.2 Acid digestion Procedures

0.5 g of each plant sample was digested in 50 ml beaker. After that 8 ml of concentrated nitric acid (65%) was added then covered with a watch glass and was left overnight at room temperature. Then 2 ml of H_2O_2 (30%) was added and heated on a hot plate (90ºC-100ºC). When the mixture was nearly dry, 5 ml of distilled water was added and covered to continue the heating process until a light yellowish colour fume is produced. Deionized water 5 ml was added and then left to cool. The samples were filtered with a hardness filter paper No.2 Whatman and placed in a 50 ml volumetric flask filled to the mark with nitric acid 0.1M and is ready to be analyzed.

2.3 Sample analysis

Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) - Perkin Elmer model 7000 DV) was used for analysis of trace metals concentration in digesting plant samples such as Fe, Cu, Zn, Pb, Ni and Cr. The trace metals concentration is found from the mean of 3 replicate ±SD of the dry sample. The instrument was calibrated daily using the Merck standard solution. The following equation has been used for calculation

$$\text{Metals }(\text{mg} / kg) = \frac{[\text{Conc.of metals }(\text{mg}/kg)\text{x Volume of sample (L)}]}{[\text{sample weight (kg)}]} \qquad (1)$$

The contamination factor (CF) used in the literature for assessment the pollution (Hakanson, 1980; Wang *et al*., 2015; Nouri, and Haddi, 2016)). The calculation of CF was from the ratio of the concentration in herbal plant (C_{sample}) dived to the background ($C_{background}$) obtained based on the permissible limit of the metal in the plant by World Health Organization Recommended (WHO) (WHO, 2011). The classification of CF values stated by Hakanson (1980) is: CF<1 entitles low pollution factor, 1≤ CF<3 moderate pollution factor, 3≤ CF>6 is considered a pollution factor, CF ≥ 6 is an abundant pollution factor.

$$CF = \frac{C_{sample}}{C_{background}} \qquad (2)$$

3. Results and discussion

The average concentrations of Fe, Cu, Zn, Pb, Ni. and Cr in Parsley (PC), Arugula (ES), Coriander (CS), Mint (ME) and Basil (OC) herbal plants were collected from different local market, Jeddah City is given in (Table 2). In addition (Figure 1) showed the average concentration of trace metals in the herbal plant sample compared with the World Health Organization Recommended (WHO). The arrangement order of trace metal in the herbal plants was found in the sequence of Zn > Fe > Ni> Cu > Pb > Cr

Fe concentration in the herbal plants samples in this study showed a range of values from 44.4 to 148.5 mg/kg as shown in (Table 2). Moreover, the Fe amount in almost all the plant samples were above the permissible limit prescribed by WHO (20 mg/kg). Fe is a standout amongst the critical components essential to the human body for the oxygen rotation in the blood. Lack of Fe can cause different sort of illnesses. However, the growth of plants can be affected by high amount of Fe element. The recorded amount of Fe in herbal plant compared with the amounts of Fe found in Egyptian spices and medicinal plants that ranged between 26.96 mg/kg and 1046.25 mg/kg, and leafy vegetable in Saudi Arabia were found 543.2 and 399.1µg/g (Abou-Arab and Abou Donia, 2000; Ali and Al-Qahtan, 2012). The clarification of this circumstance is that Fe uptake can be aggregated in the leaves because leaves are considered nutrition making manufactures in plants.

The concentration of Zn was 18.9 mg/kg in OC and 218.3 mg/kg in ES (Table 2). In the other herbal plants Zn concentration were in average of 57 mg/kg, which is slightly above the permissible limit reported by WHO (50 mg/kg). however, zinc is an essential trace element in human diet, also Zn is necessary for proper growth, and protein and DNA synthesis (Ogundele et al., 2015). Little information is available on Zn's toxicity; however, high zinc intake beyond permissible limits produces toxic effects on the immune system, blood lipoprotein levels (Ulla et al., 2012)**.** The results agree with the study obtained by Al-Hammad and Abd El-Salam (2016) for Zn level in leafy green (57.50 mg/kg) in Al-Kharj region, Saudi Arabia (Al-Hammad and Abd El-Salam, 2016).

The concentration range of Cr metal in the herbal plants samples were from 4.7 mg/kg to not-detectable, as shown in (Tables 2) while ME, CS and PC was 2.8 mg/kg, 2.1 mg/kg, 4.7 mg/kg, respectively. The Cr level was found to be higher than the allowable level which is 1.30 mg/kg according to WHO recommendation. The high Cr concentration in the herbs might be a result of distinctive of different species (Cr^{3+} and Cr^{6+}) which coming from varies natural origin and anthropogenic activities. it is a non-essential and toxic element for plant and are unfavourable to their development and growth. Cr was not detected in ES, OC due to the plant shoots uptake to the Cr is mostly low. The mean concentration of Cr determined in Al-Kharj region, Saudi Arabia in the herbal plants were found (0.195-0.431 mg/kg) which is lower than the presented study (Al-Hammad and Abd El-Salam 2016).

The mean concentration of Pb in herbal plants samples varied widely from 9.3-17.3 mg/kg, which is higher than the permissible level (2 mg/kg) recommended by WHO. Pb metal well known as a non-essential toxic for human by accumulating in the body, which cause many health problems such as, nervous and immune system, carcinogenic and learning deficiencies for children (Kananke *et al*., 2014). The Pb toxicities is found in large amounts in many electronic devices and vehicular emissions, which can end up in soil through corrosion, although Pb could deposit on the leaves through the atmosphere (Nouri, and Haddioui, 2016). Ali and Al-Qahtani (2012) studied different vegetables gathered from fundamental urban communities in the Kingdom of Saudi Arabia reported that Pb concertation (0.54-6.98 µg/mg) (Ali, and Al-Qahtani, 2012).

The mean concentration of Ni metal in herbal plants varied between 12.6- 24.4 mg/kg. The permissible limit of Ni by WHO is 10 mg/kg, all the concentration values were higher than the recommended limit. Ni has been thought to be a fundamental element for human and creature health and furthermore retained effectively and quickly by plants (Ogundele *et al.*, 2015) . The highest mean concentration of Ni in the herbal plants found for this work were higher contrast with high mean concentration of Ni stated in Al-Kharj region, Saudi Arabia (5.28 mg/kg) (Al-Hammad and Abd El-Salam, 2016). On the other hand, in Morocco reported higher amount of Ni (85 mg/kg) than this work (Al-Jaboobi *et al*., 2014).

Copper (Cu) metal occurs generally in soil, sediments and air and is a micro element, which is essential for the plant metabolism and growth. The concentration of Cu in herbal plants ranged between 15.4 to 28.6 mg/kg (Table 2), which is higher than the permissible limit according to WHO standard (10 mg/kg). This agreed with the study carried out by (Ali and Al-Qahtani, 2012) in Saudi Arabia as mentioned previously.

Table 2: The average trace metals concentration in herbal plants (mg/kg) and WHO.

sample	Fe	Zn	Cr	Pb	Ni	Cu
ME	78.5±0.06	46.1±0.26	2.3±0.002	9.3±0.31	13.7±0.064	28.6±0.26
OC	84.4±0.09	18.9±0.08	1.1±0.003	10.1±0.44	12.6±0.04	15.4±0.03
ES	108.9±1.7	218.3±1.9	ND	14.5±0.48	24.4±0.09	27.3±0.10
CS	148.5±1.8	65±0.05	4.7± 0.08	17.3±0.07	19.4±0.84	15.7±0.06
PC	44.4±0.15	57.5±0.06	2.1± 0.003	13.3±0.09	22.9±0.73	18.9±0.006
WHO	20	50	1.32	2	10	10

ND- Not detectable.

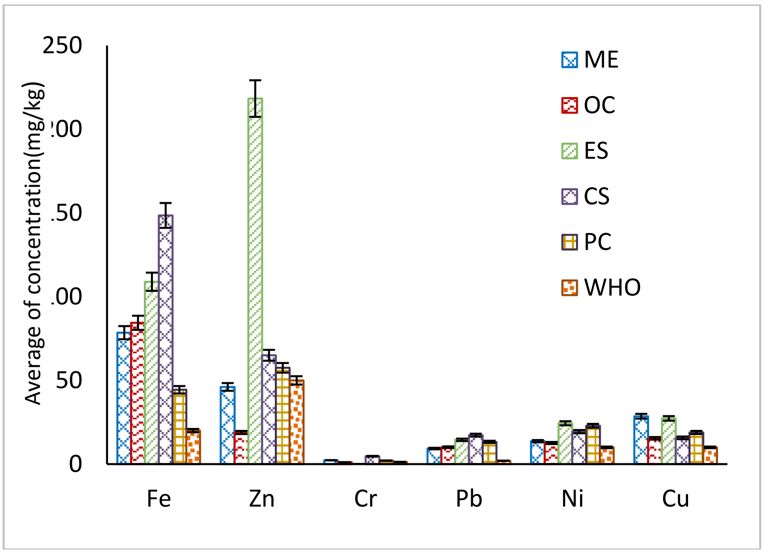
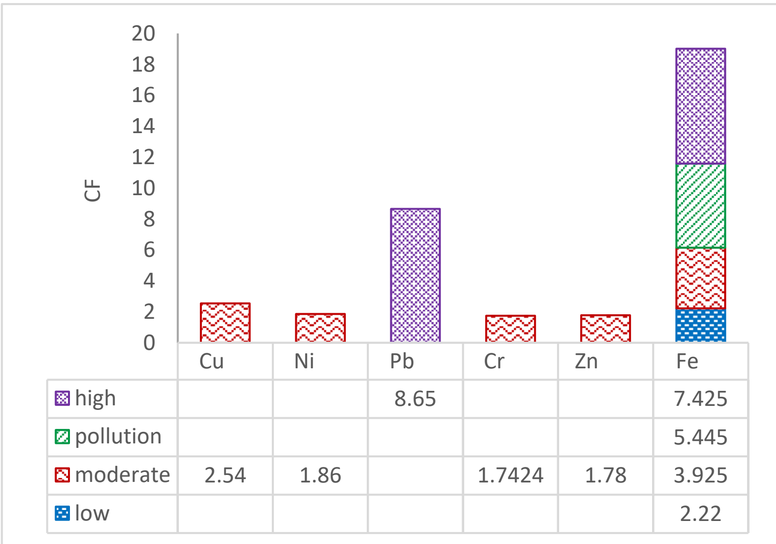


Figure 1: Average concentration of trace metals in herbal plants, WHO.



	Cu	Ni	Pb	Cr	Zn	Fe
high			8.65			7.425
pollution						5.445
moderate	2.54	1.86		1.7424	1.78	3.925
low						2.22

Figure 2: The contamination factor (CF) of trace metals in herbal plants

Figure 2 shows the contamination factor (CF) in herbal plant samples. The CFs values were 2.54, 1.86, 1.74, 1.78 for Cu, Ni, Cr, Zn respectively, indicated that the herbal plants have a moderate degree of pollution. The value of CF for Pb 8.65 and Fe 7.42 in herbal plant, which is higher than 6 that indicated a high degree of pollution. This indicates that high level of trace metals in herbal plants can lead to human health risk, moreover a study located in Sri Lanka found similar results with green vegetables collected from their local market (Kananke *et al*., 2014). Previous study has revealed that the polluted area had high level of metals in the plant than the non-polluted area (Magaji *et al*., 2018)

Trace metals have been found in herbal plants from China, Pakistan, UAE, Saudi Arabia and other Middle Eastern countries (Ernst, 2002; Ulla *et al*., 2012; Begumi *et al*., 2017; Dghaim *et al*., 2015; Maghrabi, 2014; Abou-Arab and Abou Donia, 2000), respectivaly. Based on the result, suggesting that most of the herbal plants suffering from metal pollution might be due to the planting or the way of transportation. Therefore, various factors are contributing to trace metal contamination in herbal plants as a source of agricultural soils pollution, coming from the pesticides, fertilizers, water irrigation, industrial emissions, and atmospheric deposition from town wastes (Mousavi *et al.,* 2014). On the other hand, it was confirmed that trace metals contents varied depending on mother country, ecological contamination levels, and processing techniques (Abou-Arab and Abou Donia, 2000; Abu-Darwish, 2009).

4. CONCLUSIONS

This examination demonstrated that the herbal plants may represent a well being danger to the general population who eat them as they were observed to be insufficient of essential metals, for example, Fe, Zn, and Ni. Then again, they were found to have higher than permissible limits of metals from WHO standard in example Cu, Ni, Zn, and Cr. Besides, the herbal plants were additionally found to have a large amount of harmful metals, for example, Pb and Fe. More consideration should be taken in to account to control and check pollution levels in herbal plants. Additionally, from this point considering an action for new study has settled to explore the contamination levels of the trace elements in herbal plants and their correlation between the soil, water irrigation, pesticides, and fertilizers,

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