Bio-accumulation of Aluminum in Fruits Grown in Contaminated Agricultural Soils

Awad A. Momen*

Department of Science and Technology, University College-Ranyah, Taif University, KSA

a.abdelkareem@tu.edu.sa

Keywords: *Aluminum, ICP-OES, Plants, Potentially toxic elements, Soils, Soil-plant-transfer-factors.*

Assessment the transfer of aluminum (Al) from potentially contaminated agricultural soils and bio-accumulation in fruits was the main focus of current study. After determination of Al concentration in soils and fruits, soil-plant-transfer-factors (SPTF) were calculated and compared to those reported in related studies. Obtained Al concentrations were compared to acceptable limits that given by FAO/WHO. Soil samples include surface soils (s) and depth soils (d), while fruit samples include cantaloupe melon, grape, pomegranate and mandarin. Samples were digested by microwave-assisted oven and Al concentrations were determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES). Results indicates that Al concentrations in soils were high (>50.22mg/Kg) than in fruits (<0.947mg/Kg). Results revel that Al concentrations in studied fruits were low than the maximum permissible concentrations in fruits given by FAO/WHO. Despite this concentration, caution must be taken regarding presence of high Al in soils and fruits. Calculated SPTF values for Al were relatively low (<0.0134), this confirm that the general ability of Al to bio-accumulate was relatively limited.

Introduction

Soil, a main part of the terrestrial ecosystem, is a heterogeneous mixture of different organisms and minerals, organic, and organo-mineral substances present in three phase, liquid, solid and gas [1]. At same time, soil is perhaps the most endangered component of our environment open to potential contamination by a variety of different pollutants arising from human activities such as industrial, agricultural, etc [2].

Contamination of soils with potentially toxic elements (PTE) in agricultural areas has always received great attention to human health. Even at low concentrations the presence of PTE like Al in environment can cause toxicity to both plants and animals [3-4].

Human activities sometimes contribute impacts to the environment in order to meet their needs; these impacts can be either positive and/or negative. Positive impacts on the environment include reforestation, using clean energy, and protecting natural preserves and forests to maintain the natural biodiversity. While negative impacts due to human activities decline environment quality, such as soil degradation due to waste pollution produced by household, industrial and agricultural activities [5]. One of the most impactful pollution and/or contaminants for soils and plants is PTE. These contaminants infiltrate into soils and plants and increase toxicological effect because soils were closely related to agriculture activities [6].

Growing population-related food demand has resulted in a significant rise in the use of agricultural chemicals; these chemical materials were inherently containing PTE. Since PTE were persistent, non-biodegradable and toxic to living organisms, soil pollutions were major concern. Their mobility and bioavailability were also impacted by the different soluble and particulate materials in which they were found [7].

Aluminum (Al) is the most commonly occurring metallic element, comprising 7.0% of the earth's crust. At neutral or weakly acidic pH, Al exists in form of insoluble minerals of aluminum oxides and aluminosilicate clays [8, 9]. Once soil pH<5.5, their minerals begin to dissolve, releasing aluminum-hydroxy cations and $[Al(H_2O)_6]^{3+}$, that exchange with other cations from soil colloids. The fraction of exchange sites occupied by $[Al(H_2O)_6]^{3+}$ and its hydrolysis products can become large once the soil pH falls <5.0. Furthermore, as the pH is lowered, the concentration of soluble Al will also increase [10-12].

Moreover, Al may be an essential in the trace level but access amount may be leading to toxic effects for humans, flora and fauna. High levels of Al in the human body can pose a serious threat to health [11].

Soil-plant system has three protective mechanisms which may limit the potential toxicity of heavy metals in plants and thus reduce the problems they might cause living beings. Furthermore, soil-plant-transfer-pathway is one of the key components of human exposure to metals through food-chain-pathway. In this study, SPTF for various metals and for most common vegetables consumed by human being were calculated. Moreover, the bio-accumulation of heavy metals in agricultural land was related to human activities and on environmental conditions [13, 14].

Assessment the transfer of Al in potentially contaminated agricultural soils and bio-accumulation of Al in fruits that grow in the study area (Agriculture soils of Wadi Turabah) was the main focus of the current work.

Experimental part

Instrumentation and reagents

The sample digestions were carried out using a microwave digestion system (Model MARS-5, CEM corporation, Matthews, USA) that is programmable for time and power between 800-1600W and equipped with 12 high pressure Teflon vessels (Model Easy Prep xp-

1500 plus, CEM corporation, Matthews, NC, USA). The heating programs for the digestion system were presented in Table 1. Furthermore, for standards and samples analysis in this study, a quadruple Elan DRCII (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA) ICP-OES (Perkin Elmer Model Optima 2100DV, USA) with CCD detector was utilized. The working environment of ICP was also outlined in Table 1. These settings were meticulously chosen and highly refined to enhance the sensitivity towards the targeted elements and to achieve the highest level of precision and accuracy. Additionally, certain essential operating parameters of MARS-5 and ICP were adjusted following the instructions provided by the manufacturer.

All the reagents were of the highest commercially available purity grade. Distilled water (18MΩ/cm) was obtained from a Milli-Q Plus water purification system (Millipore Inc., Paris, France) and used throughout the experiments. 30%H_2O_2 (d=1.11kg/L) and 65%HNO_3 (d=1.40kg/L), [Merck, Germany] were used as received for digestion of fruit samples. High-purity grade-V, atomic spectroscopy standard solution contains 200mg/L Al was purchased from PerkinElmer. This method was applied for establishing norms for calibration curves and the injection of certain samples for recovery experiments. The contaminants in the Ar and N_2 used in this research were >1%(v/v). Every piece of lab glassware was immersed in 10%(v/v) HNO_3 for a day, then rinsed multiple times with highly purified deionized distilled water before being heated in a microwave oven (KION group AG, Frankfurt, Germany).

Sampling area

The area of study (Wadi Turabah) was composed of farms located in the western part of KSA (Makkah region). The geographical coordinates of Wadi Turabah lie at longitude and latitude of 41° 37'59" E and 21°12'51" N respectively and at an elevation of 1164m (3819Ft) above sea level. It extends over a length of 400km with a hot deserts climate [15]. This area was considered one of the most fertile valleys in the western region of the KSA. Soils of this area were sandy to fertile clay and seasonal plants such as watermelon and tomatoes grow in it, in addition to perennial plants such as palm dates.

Fruits sampling and treatments

Twelve fruits samples of highly consumed varieties were collected from different agricultural farms located in Wadi Turabah. Samples include cantaloupe melon, grape, pomegranate and mandarin. Samples were collected in clean polyethylene containers according to their types. After collection the outer surface of fruits was first washed with distilled water, then air dried and kept in the refrigerator before processing with the drying and digestion process.

For the drying process, samples of each type were firstly cut separately with a clean stainless-steel knife into small pieces (2-3mm size). Then mixed thoroughly and placed in an oven at 102°C until a constant weight was reached. Three dried samples of each type were mixed, ground to a fine powder and homogenized using a clean commercial kitchen grinder. Specimens that were ground were properly graded and stored in polyethylene containers at -20°C until needed for analysis [16].

For digestion 0.50g of each sample was accurately weighed into a PTFE digestion vessel and introduced into a Teflon digestion vessel of microwave assisted oven. 2.0mL H_2O_2 and 4.0mL HNO_3 were added to each sample. The contents were carefully shaken, then the digestion vessels were well closed and optimum heating programs were followed. After digestions were completed, the contents of the vessels were quantitatively transferred to a 50mL volumetric flask and diluted to the mark with distilled water. This procedure was almost similar to the one mentioned in our previous work with some modifications. Also, many analytical blanks were prepared in the same way as samples were prepared for characterization of instrumental drift [17].

Soils sampling and treatments

Eighteen soil samples were collected from six sampling points of corresponding area where the fruits were grown. Soils were taken from a surface (s) and depth (d) of 25.0cm long using a hand-held polyethylene spoon after the autumn season. Three samples from each point (500g) were reduced to one representative sample by cone and quarter. Samples were then dried at 102ºC, then ground to pass through a 63μm nylon sieve and transferred to polyethylene bottles, stored at room temperature (27°C) until needed for analysis [16].

For digestion 0.50g of each sample was accurately weighed into a PTFE digestion vessel and introduced directly into a Teflon digestion vessel of microwave assisted oven. 1.0mL H_2O_2, 2.0mL HCl, 3.0mL HF and 9.0mL HNO_3 were added to each sample. Then the same methods for fruit digestions were followed until the end. This procedure was almost the same as the one mentioned in our previous work with some modifications. Also, several analytical blanks were prepared in the same way as samples so as to characterize instrumental drift [15].

SPTF determination

The transfer ability of metal from soils to plants was studied using an indicator called SPTF. It regarded as one of the most important parameters in environmental safety assessment needed for soil contaminations. It depends upon many factors such as: pH, electrical conductivity (EC), and bicarbonate contents of soil, etc. In addition, organic fertilizer affects the ion exchange capacity, stable element content of soil, as well as soil retention properties. This parameter was necessary for environmental transfer models which were useful in prediction of the contamination in agriculture soils. It's calculated as the ratio of the concentration of a specific metal in the fruit to the concentration of same metal in the soil where the fruit was grown (both represented in same concentration units).

If SPTF>1, indicates high uptake of metal by fruits, while SPTF=1 indicate that the fruits were not affected by the elements and SPTF<1 indicates that fruits exclude the elements from absorption. If the plants have higher SPTF values, it may be good if they were used for element-extraction and phytoremediation. On the contrary, lower values indicate a poor response of plants to metal absorption and the plant can be used for human consumption [14, 18].

Calibrations

About seven standard solutions were prepared by diluting a multi-element standard solution containing Al. Blanks were prepared in the same way as the standard solutions and the calibration curve was plotted for Al.

Statistical analysis

The results were statistically evaluated by ANOVA and Student *t-test*, ($P<0.05$), in addition to Microsoft Excel and Origin programs. In this study all statistical analysis were based on triplicate measurements [19].

ICP-method validation

To evaluate the analytical methods used to analyze Al in fruits and soils by ICP-technique, some analytical figures of merit were estimated. These include spectral emission lines (wavelengths), linearity, accuracy, precision, LOD and LOQ. The analytical wavelengths (nm) for Al were set at the primary (atomic) and secondary (ionic) lines. For linearity the square correlation coefficient (R^2) was determined by preparing the calibration curve using the non-weighted least-squares linear regression line.

Moreover, in order to know the accuracy of the analytical methods the recovery (%) were measured by spiking some fruit and soil samples with standard solution and passing them through the same digestion procedure. While, the precision of analytical methods were estimated by calculating the relative standard deviation (RSD). The LOD and LOQ were calculated for Al as follows:- $LOD=3\sigma/m$, $LOQ=10\sigma/m$, whereas, (σ) is the standard deviation of intensity of seven blanks and (m) is the slope of calibration curve for Al [19].

Determination of Al in fruits and soils

All standards and sample solutions were analyzed three times on a Varian 710ES axial ICP with a CCD detector. The Cetac automatic sampler with 15mL sample tubes was connected to the peristaltic pump. A Burgener Teflon Mira Mist (SCP Science) nebulizer and a glass cyclonic spray chamber were used to introduce standard and sample solutions). The concentrations of Al were determined in digested fruit and soil samples by ICP using the optimum instrumental parameters.

Results and discussion

Microwave parameters optimization

The efficacy of sample digestion depends on sample matrix, so it was important to optimize the microwave oven conditions. The temperature of the microwave oven and the acid/oxidant mixture further effects sample digestion, while, pressure, ramp, holding and ventilation time have relatively small effects. The microwave oven temperature was set between 210-260ºC, a clear solution was observed at 220 and 250ºC for fruits and soils, respectively. Therefore, oven temperature at 220 and 250ºC were used in this study.

Moreover, the acid/oxidant mixture (H_2O_2/HNO_3) has been studied in a ratio of 1:1, 1:2, 1:2, 1:3 and 1:4, a clear solution was observed in a ratio of 1:2. Therefore, a ratio 1:2 was used to digest fruit samples throughout this study. While an acid/oxidizing mixture ($H_2O_2/HCl/HF/HNO_3$) in a ratio of 1:1:2:2, 1:2:4:8, 1:2:3:9, 1:3:5:7 and 1:4:6:9 was studied. A clear solution was observed in the ratio of 1:2:3:9, therefore, this ratio (1:2:3:9) was used to digest the soil samples during this study. The optimal values of microwave oven parameters were shown in **Table 1**.

Table 1. MARS-5 heating program for digestion of fruits and soils

Condition	Used values
Temperature[a]	220 and 250°C for fruit and soil samples respectively
Pressure	800(pis)
Ventilation	10(min)
Holding time	10(min)
Ramp time	25(min)

[a]Optimized value

ICP parameters optimization

Since the signal intensity for Al was depends on the sample matrix, it's important to optimize the ICP-parameters. The emission intensity was mostly affected by radio frequency (RF) incident, Ar gas nebulizer flow rate and sample uptake flow rate that have a greater influence on the measurement sensitivity. Whereas frequency, plasma and auxiliary Ar-gas flow rate have relatively small effects on sensitivity and were adjusted to accommodate memory effects due to a particular sample type such as organic materials and/or TDs. The radio frequency (RF) incident power was studied in the range 1400-1800W. The results indicate that sensitivity and linearity were better at 1600W and improve plasma stability [20].

In addition, the effect of nebulizer Ar-gas flow rate was studied between 0.40-0.80L/min. A maximum intensity of 0.60L/min was observed, thus a flow rate of 0.60L/min of nebulizer Ar-gas was adopted throughout this study, providing good precision and high sensitivity. Furthermore, the sample uptake flow rate was investigated at three levels: 1.0, 2.0 and

3.0mL/min. It was found that the emission intensity was slightly higher at 2.0mL/min. Therefore, sample uptake flow rate of 2.0mL/min was chosen for this study, which provides sufficient sensitivity and low sample consumption (**Table 2**).

Spectral lines selection

Al was measured in two different spectral emission lines (atomic and ionic line). The criteria for choosing between them were based on the sensitivity, spectral interferences and concentration range of Al. In all cases, sensitivities were calculated on spectral lines with lower interferences and high sensitivity. The specific selected line (nm) for Al was indicated in **Table 2**.

Table 2. ICP-instrumental conditions

Parameters	**Selected values**
RF-incident power[a]	1600W
Frequency	40.68MHz
Nebulizer Ar-gas flow rate[a]	0.60L/min (Ar-gas)
Plasma Ar-gas flow rate	15.0L/min (Ar-gas)
Auxiliary Ar-gas flow rate	0.2L/min (Ar-gas)
Sample uptake flow ratea	2.0mL/min
Wavelengths for Al[a]	308.212nm

[a]Optimized value

Analytical figures of merits

The selected spectral lines that give high sensitivities and maximum emission intensities under optimal ICP operating conditions. Furthermore, the linearity of the method was tested using the selected analytical line were determined at five concentrations in range 0.04-100mg/L. That was satisfactory for Al, R^2>0.9992 in linear regression lines. This confirms the linearity of the analytical method used according to the standards set by the AOAC [21].

Furthermore, the accuracy of the analytical method was calculated as recovery (%), and it was found to be within the acceptable range [Spiking recoveries(%)=100±4]. This indicates that there were no significant losses and/or gains for Al using the developed technique. In addition, the precision of ICP-method was calculated as RSD of five independent replicates for each sample <3%. Moreover, the LOD of the Al=0.0556mg/kg, while LOQ=0.174mg/kg. Obtained values (LOD and LOQ) clearly demonstrated the high sensitivity and the linear range of the ICP-method.

Concentration of Al in fruits and soils

ICP-method was used to identify Al in four varieties of the most commonly consumed fruits in Turabah governorate and other regions in KSA. In addition, soils of farmers' land where fruits were grown were also evaluated. The concentrations (mean, dry weight) of Al were shown in **Table 3** (fruits) and **Table 4** (soils).

Table 3. Aluminum concentrations in fruit samples

Fruits samples (English name / *Scientific name*)	Concentration of Al (mg/Kg)[a]
Cantaloupe melon/*Cucumis melo var. Cantalupensis*	0.917±0.072
Grape/*Vitis vinifera*	0.947±0.088
Pomegranate/*Punica granatum*	0.258±0.051
Mandarin/*Citrus reticulate*	0.935±0.074
Mean value	**0.764±0.071**
Acceptable limits by WHO/FAO for all Al compounds in food [22]	**2.0**

[a]Results were expressed as mean±standard deviation, [a]Analysis based on dry weight of the edible portion (n=3)

The analyzed Al content in fruits (**Table 3**) showed different concentrations of Al in fruits samples with mean value of 0.764±0.071mg/Kg. Higher concentration of Al was found in grape (0.947±0.088mg/Kg), while the lower concentration was observed in pomegranate (0.258±0.051mg/Kg). Furthermore, the results (**Table 3** and **Figure 1**) showed no significant differences ($P<0.05$) were observed regarding Al concentrations in studied fruit samples. The concentrations of Al in studied fruits were in the order: grape>mandarin>cantaloupe> pomegranate (**Table 3** and **Figure 1**). However, the general concentrations of studied Al in fruits from Turabah farms were lower than the maximum permissible concentrations of fruits given by the FAO/WHO [23-25].

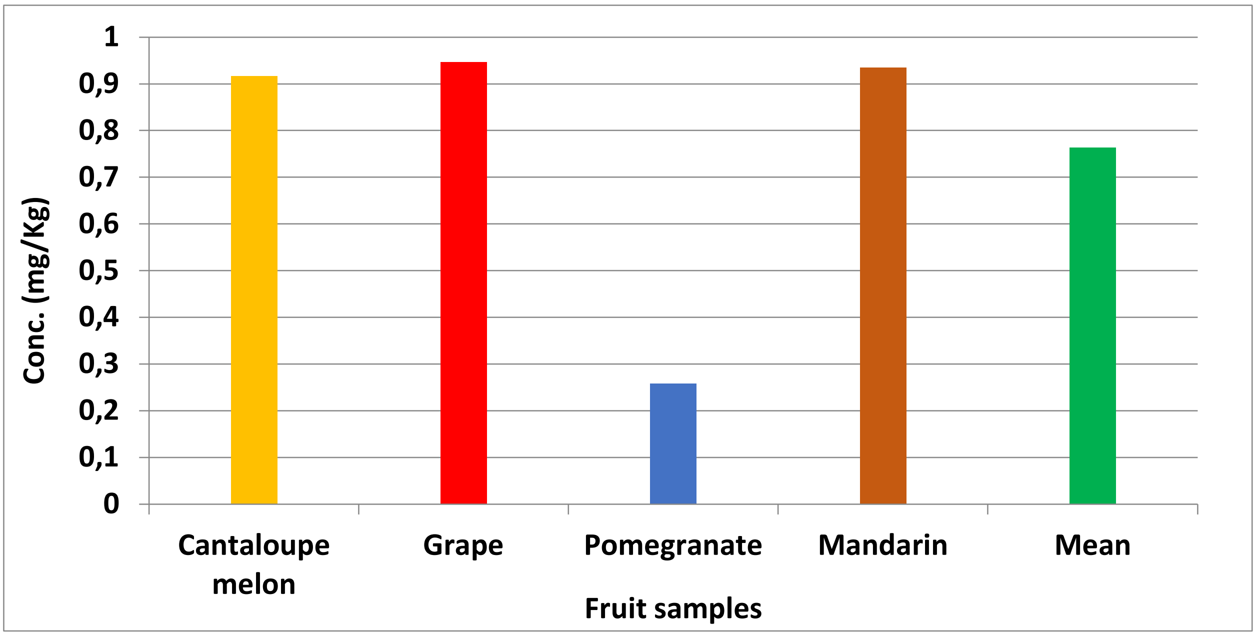

Figure 1. Aluminum concentrations in fruit samples

Table 4. Aluminum concentrations in soil samples

Soil samples	Concentration of Al (mg/Kg)[a]
s(i)	80.54±3.55
s(ii)	104.2±4.78
s(iii)	50.22±2.89
d(i)	60.14±3.03
d(ii)	51.38±3.11
d(iii)	76.98±3.71
Mean value	**70.58±3.51**
Acceptable limits by WHO/FAO [23-25]	**50-140**

[a]Results were expressed as mean±standard deviation, [a]Analysis based on dry weight of the edible portion (n=3)

There were references for metal concentration in soil around the world, for example, Al concentration in soils=1.0-6.4% [5]. In this study, we identified that Al concentration in studied soil samples were still between (50.22-104.2mg/Kg).

Table 4 showed different concentrations of Al in all samples. High concentrations of Al were recorded in s(ii)=104.2mg/kg, while low one was recorded in s(iii)=50.22mg/kg. The bio-accumulations of Al were in the order: s(ii)>s(i)>d(iii)>d(i)>d(ii)>s(iii) (**Table 4** and **Figure 2**). Moreover, the results (**Table 4**) indicated no significant differences ($P<0.05$) were observed regarding the concentrations of Al in the different studied soil samples. Mean concentration of Al in fruits and soils=0.764±0.071mg/kg and 70.58±3.51mg/kg respectively.

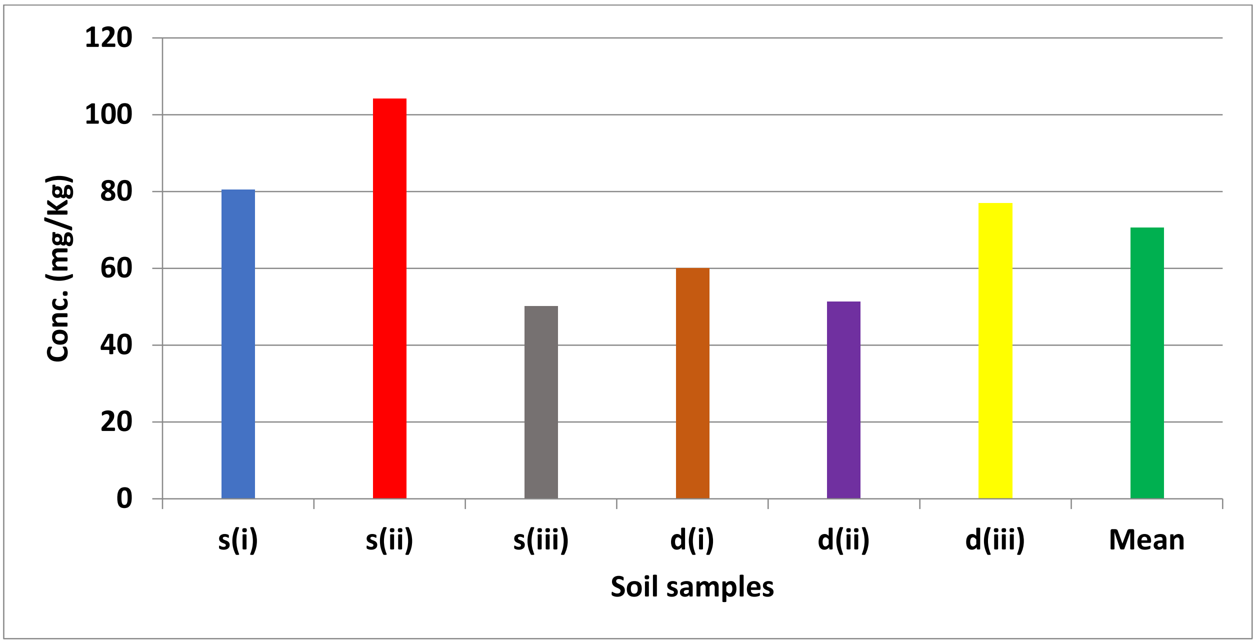

Figure 2. Aluminum concentrations in soil samples

Figure 3 indicated that the mean concentration of Al was very high in soils (70.58±3.51mg/kg) than in fruits (0.764±0.071mg/kg). Many observations were reported by Dilek and Ahmet [26], Govind and his group [27] and Nwajei and his group [28] concerning about Al concentrations in soils and fruits. They conclude that Al concentrations were always high in soils than in fruits especially in neutral or weakly acidic soils (pH>5.5). Once soil pH<5.5, the concentration of soluble Al will also increase, in this case the uptake of Al by may also increase by plants (fruits) [10-12].

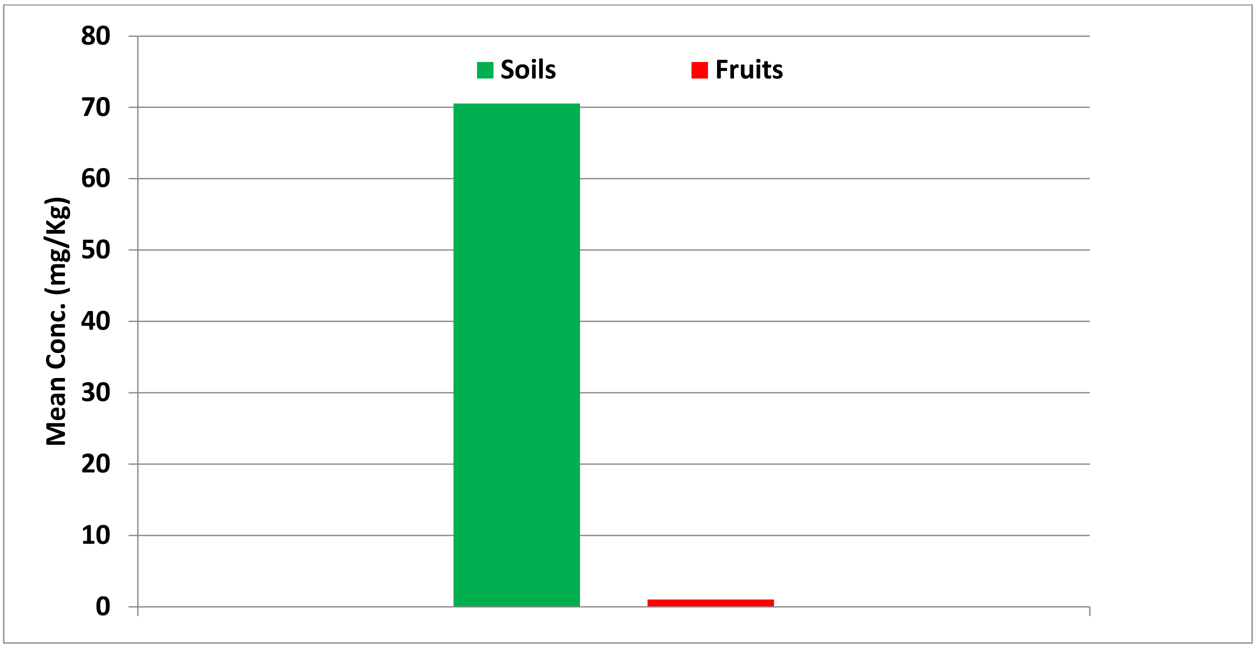

Figure 3. Mean concentrations of Al in fruit and soil samples

Physico-chemical properties of soils

The physic-chemical properties of soil like pH, conductivity, bulk density, organic matter (%), organic carbon (%), moisture content (%) were a significant determining factors. The total concentration of metal soils and several other factors affect the concentration of free metal ions. The examined soils had a sandy loam texture and it's impacted by the interaction of nearby organic and inorganic materials with CO_2 from atmosphere. The pH of the soils must be at the required level for healthy development and effective uptake of nutrients from the soils [29, 30].

Determination of SPTF

Elements were absorbed by plant roots from soil and then distributed in various plant tissues like stems and fruits. The mobility and uptake of elements from soils to plant tissue (fruits) was measured by an index called SPTF. Its calculated as a ratio of concentration of a specific element in plant tissues (fruits) to the concentration of same element in the soils, using the following equation [18, 31-35]:

$$SPTF = \frac{Concentration\ of\ Al\ in\ plant\ friut}{Concentration\ of\ Al\ in\ corresponding\ soil}$$

SPTF is one of simple way to explain human exposure to elements through the food chain. SPTF for each particular element can vary greatly depending on elements chemistry, plant bio-disponibility, and type of plants and analyzed part of plants. Also the main parameters that modify SPTF were physical and chemical characteristics of soils, concentration and behavior of elements in soils and plants and the environmental changes [36-38].

Their values (**Table 5**, **Figure 4**) reflect the actual ability of fruits to take up Al from soils. If SPTF≥1, this indicate that high Al absorption by plants and that may causes harm to human health. On the contrary, low SPTF values (>1) indicate poor plant response toward metal absorption and plants can be used for human consumption without health risks. However, if SPTF>1, it cannot be concluded that soils were the only source of PTE contamination in plants, they may be environmental factors [18, 39].

Table 5. Soil-plant-transfer-factors of aluminum

SPTF (present study)					**SPTF (reported in literature)**
Cantaloupe melon	Grape	Pomegranate	Mandarin	Mean value	
0.0123	0.0134	0.004	0.0132	0.0107	0.0000023-0.00040 [4]; 0.011 and 0.067 [5]; 0.0002-0.097 [40]

Calculated values were reported in dry-by-dry basis

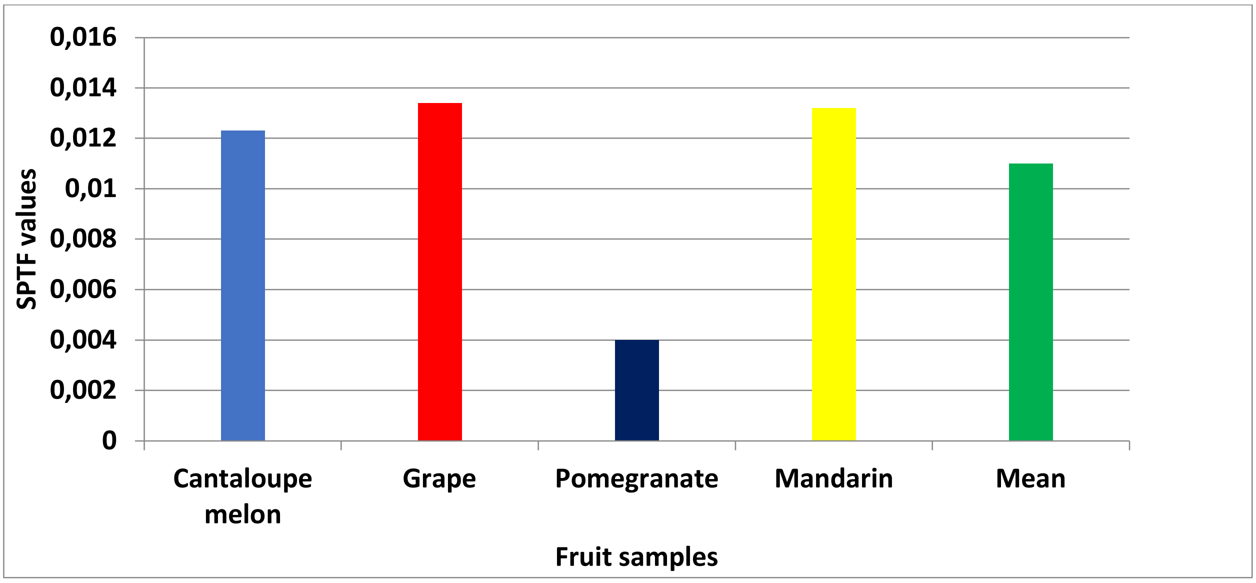

Figure 4. Soil-plant-transfer-factors of aluminum

SPTF values depend upon many factors such as pH, EC, and HCO_3^- contents of soil, etc. Soil samples under study were geologically the same and the climatic conditions were approximately similar. Organic fertilizer affects the ion exchange capacity, stable element content of soil, as well as retention properties of soils [41, 42].

Results (**Table 5**) revels that grape had high ability to absorb and bio-accumulate Al (SPTF=0.0134) more than other fruit samples, while pomegranate had low ability (SPTF=0.0040). Moreover, SPTF values of Al from soils to fruits show the following trend: grape>mandarin>cantaloupe melon>pomegranate (**Table 5** and **Figure 4**).

Results indicate that grape, mandarin and cantaloupe melon have highest SPTF values than pomegranate; this may be due to some anthropogenic activates.

A study by Vandenhove et al., [43] revealed that element like Al may has much low SPTF values, this due to high affinity of Al with soil particles, resulting in minimal uptake Al by plants. Chandrashekara et al., [44] recommended that small uptake of Al could result from Al behavior; plants may transport Al along with Ca.

Conclusions

The current study was aimed to study the concentration of Al in soils and fruits in order to determine the ability of Al to bio-accumulate in certain fruit samples grown on the same soils areas. SPTF were used as a parameter for assessment of bio-accumulation of elements from soils to plants. The results of this study indicate that the concentrations of Al in fruits (≈0.947mg/Kg) and soils (≈50.22mg/Kg) from studied areas were low than the maximum permissible concentrations limit that given by FAO/WHO. Calculate SPTF values were in the range 0.003-0.0135, this implies that the general ability of Al to bio-accumulate was very low. The results confirm that the plants in the study areas were safe and can be used for human conceptions without any health risks. In order to keep our foods clean i recommend that the concentration of Al in soils of the study areas must be at low level as much as possible in order to avoid Al bio-accumulation.

Acknowledgements

The author would like to acknowledge Deanship of Graduate Studies and Scientific Research, Taif University for funding this work.

References

[1] CoŞKun M, Steinnes E, Frontasyeva M, Sjobakk T, Demkina S. Heavy Metal Pollution of Surface Soil in the Thrace Region, Turkey. Environmental Monitoring and Assessment 2006;119(1-3):545-556.

[2] Kalantari M, Shokrzadeh M, Ebadi A, Mohammadizadeh C, Choudhary M, Rahman A. Soil Pollution by Heavy Metals and Remediation (Mazandaran-Iran). Journal of Applied Sciences 2006;6(9):2110-2116.

[3] Rana M, Halim M, Safiullah S, Mollah M, Azam M, Goni M, Hossain M, Rana M. Removal of Heavy Metal from Contaminated Water by Biopolymer Crab Shell Chitosan. Journal of Applied Sciences 2009;9(15):2762-2769.

[4] Uchida S, TagamiI K, Hirai I. Soil-to-Plant Transfer Factors of Stable Elements and Naturally Occurring Radionuclides: (2) Rice Collected in Japan. Journal of Nuclear Science and Technology 2007;44(5):779-790.

[5] Prabasiwi D, Sukirno, Murniasih S, Rozana K. Transfer factor as indicator of heavy metal content in plants around adipala steam power plant. Journal of Physics: Conference Series 2020;1436(1):012133.

[6] Kumar A, Ahirwal J, Maiti K, Das R. An Assessment of Metal in fly Ash and Their Translocation and Bioaccumulation in Perennial Grasses Growing at the Reclaimed Opencast Mines. Int. J. Environ. Res. 2015:9;1089-1096.

[7] Tomer N. Determination of chlorinated pesticide in vegetables, cereals and pulses by gas chromatography in East National Capital Region, Delhi, India. Res. J. Agri. Forest. Sci. 2013;1(1):27-28.

[8] Filiz V, Meral Ü. Review: Aluminum toxicity and resistance in higher plants. Advan. Mole. Bio. 2007;1:1-12.

[9] Jolly Y, Islam A, Akbar S. Transfer of metals from soil to vegetables and possible health risk assessment. SpringerPlus 2013;2(1):385-392.

[10] Chiroma M, Ebewele O, Hymore K. Levels of Heavy Metals (Cu, Zn, Pb, Fe and Cr) in Bush green and Roselle Irrigated with Treated and Untreated Urban Sewage Water. Int. Res. J. Environ. Sci. 2012;4:50-55.

[11] Ebnesajjad S. Characteristics of Adhesive Materials. Handbook of Adhesives and Surface Preparation 2011:137-183.

[12] Tomas J, Arvay J, Toth T. Heavy metals in productive parts of agricultural plants. J. Micro. Biotech. Food Sci. 2012;1:819-817.

[13] Nasrin C, Mamunur R. Heavy metal contamination of soil and vegetation in ambient locality of ship breaking yards in Chittagong, Bangladesh. J. Environ. Sci. Toxic. Food Techno. 2016;10:20-27.

[14] Nataša M, Rukie A, Ljubomir Š, Lidija M, Zoran I. Transfer Factor as Indicator of Heavy Metals Content in Plants. Fresenius Environ. Bulletin. 2015;24:4212-4219.

[15] Elsheikh M, Hassan Mahmoud M, Momen A. Determination of Selected Toxic Trace Elements in Agricultural Soil and Wells Water Samples by ICP-OES. Oriental Journal of Chemistry 2017;33(5):2263-2270.

[16] Inuwa M, Aina O, Baba G, Aimola I, Veronica T. Determination of Differences in Nutrient Composition of Citrullus vulgaries (Water Melon) Fruits after Plucking. British J. Dairy Sci. 2011;2:7-30.

[17] Momen A, Mahmoud M, Hag Ali D, Alotaibi S, Khalid M, Elsheikh M. Validation of Microwave and ICP Parameters for Assessment of Selected.

[18] Toxic Trace Elements in Fresh Fruits from Turabah Valley of Saudi Arabia. Asian Journal of Chemistry 2019;31(12):2793-2800.

[19] Rangnekar S, Sahu K, Pandit G, Gaikwad B. Accumulation and Translocation of Nickel and Cobalt in Nutritionally important Indian vegetables grown in artificially contaminated soil of Mumbai. Indian Res. J. Agri. Forest. Sci. 2013;1:15-21.

[20] James M, Jane M, Robert M. Statistics and Chemometrics for Analytical Chemistry, Trans-Atlantic Publs Inc. Pearson Education Limited: UK, 7th edn. 2018:1-312.

[21] Momen A, Zachariadis G, Anthemidis A, Stratis J. Investigation of four digestion procedures for multi-element determination of toxic and nutrient elements in legumes by inductively coupled plasma-optical emission spectrometry. Analytica Chimica Acta 2006;565(1):81-88.

[22] AOAC International, JAOAC Int., 22nd edn., Oxford University Press, 2023.

[23] Joint FAO/WHO Food Standards Programme Codex Committee on Contaminants in Foods 12th Session, Utrecht, the Netherlands, 12 - 16 March 2018.

[24] Elbagermi M, Edwards H, Alajtal A. Monitoring of Heavy Metal Content in Fruits and Vegetables Collected from Production and Market Sites in the Misurata Area of Libya. ISRN Analytical Chemistry 2012;2012:1-5.

[25] Yami S, Chandravanshi B, Wondimu T, Abuye C. Assessment of selected nutrients and toxic metals in fruits, soils and irrigation waters of Awara Melka and Nura Era farms, Ethiopia. SpringerPlus 2016;5(1):1-12.

[26] Vincent O, Samuel A, Iloba N, Friday O. Occurrence and Concentration of Heavy Metals in Garden Egg, Tomatoes, Cucumber and Watermelon in Edo State, Nigeria. Food Public Health 2020;10:63-67.

[27] Demirezen D, Aksoy A. Heavy Metal Levels In Vegetables In Turkey Are Within Safe Limits for Cu, Zn,

Ni and Exceeded for Cd and Pb. Journal of Food Quality 2006;29(3):252-265.

[28] Mawari G, Kumar N, Sarkar S, Daga M, Singh M, Joshi T, Khan N. Heavy Metal Accumulation in Fruits and Vegetables and Human Health Risk Assessment: Findings From Maharashtra, India. Environmental Health Insights 2022;16:1-13.

[29] Nwajei E, Okwagi P, Nwajei I, Obi-Iyeke E. Analytical Assessment of Trace Elements in Soils, Tomato Leaves and Fruits in the Vicinity of Paint Industry, Nigeria, Res. J. Recent Sci. 2012;1(4):22-26.

[30] Mohammed S, Mohammed B. Analysis of Dumpsite soil pH in selected Dumpsites of Kaduna Metropolis, Nigeria. Inter. Res. J. Environ. Sci. 2012;3:52-54.

[31] Parihar S, Kumar A, Kumar A, Gupta N, Pathak M, Shrivastav A, Pandey C. Physico-Chemical and Microbiological Analysis of Underground Water in and Around Gwalior City, MP, India. Res. J. Recent Sci. 2012;6:62-65.

[32] Akande O, Ajayi A. Assessment of Heavy Metals Level in Soil and Vegetables Grown in Peri-Urban Farms around Osun State and the Associated Human Health Risk. International Journal of Environment, Agriculture and Biotechnology 2017;2(6):3250-3261.

[33] Ogoko C. Accumulation of Heavy Metal in Soil and Their Transfer to Leafy Vegetables with Phytoremediation Potential. Amer. J. Chem. (5) 2015;5:125-131.

[34] Singh R, Singh P, Kumar N, Bhargava K, Barman C. Accumulation and translocation of heavy metals in soil and plants from fly ash contaminated area. J. Environ. Bio. 2010;31:421-430.

[35] Babuskin S, Yessuf A, Hameed O. Monitoring and assessment of the potential health risks associated with the toxic heavy metals content in selected fruits grown in Arba Minch region of Ethiopia. International Journal of Environmental Analytical Chemistry 2020;102(17):4941-4952.

[36] Yeasmin J, Ashraful I, Shawkat A. Transfer of metals from soil to vegetables and possible health risk assessment. SpringerPlus 2013;2:385-392.

[37] Cervantes-Trejo A, Pinedo-Álvarez C, Santellano-Estrada E, Cortes-Palacios L, Rentería-Villalobos M. Distribution of Chemical Species in the Water-Soil-Plant (Carya illinoiensis) System near a Mineralization Area in Chihuahua, Mexico—Health Risk Implications. International Journal of Environmental Research and Public Health 2018;15(7):1393.

[38] Zhang F, Romheld V, Marschner H. Release of zinc mobilizing root exudates in different plant species as affected by zinc nutritional status. Journal of Plant Nutrition 1991;14(7):675-686.

[39] Kadovic R, Belanovic S, Obratov-Petkovic D, Bjedov I, Dragovic N. Assessment of heavy metal content in soil and grass lands in national park of the lake plateau of the N.P. “Durmitor” Montenegro. African J. Biotechno. 2011;26:5157-5165.

[40] Yan X, Zhang F, Zeng C, Zhang M, Devkota L, Yao T. Relationship between Heavy Metal Concentrations in Soils and Grasses of Roadside Farmland in Nepal. International Journal of Environmental Research and Public Health 2012;9(9):3209-3226.

[41] Uchida S, TagamiI K, Hirai I. Soil-to-Plant Transfer Factors of Stable Elements and Naturally Occurring Radionuclides (1) Upland Field Crops Collected in Japan. Journal of Nuclear Science and Technology 2007;44(4):628-640.

[42] Hassin M, Hassan Abd M, Gomoa A, Muftah E. Integrated Effect of Fertilizers on Soil pH, EC and Organic Matter Content. Journal of Pure & Applied Sciences 2022;21(4):323-328.

[43] Tomislav K, Tomislav Ć, Boris L, Tea H, Marko P, Igor P, Nevenka J. Effect of Organic Fertilizers on Soil Chemical Properties on Vineyard Calcareous Soil. Agri.Conspectus Sci. 2015;80:79-84.

[44] Chandrashekara K, Somashekarappa H. Estimation of radionuclides concentration and average annual committed effective dose due to ingestion for some selected medicinal plants of South India. Journal of Radiation Research and Applied Sciences 2016;9(1):68-77.