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# Effect of Physicochemical Parameters of Soils on Transfer and Bioaccumulation of Potentially Toxic Elements in Plants, Wadi Turabah

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#### Abstract

Transfer and bioaccumulation of elements within soil-plant-chain (SPC) is part of the biochemical cycling of elements. The physicochemical properties of soils indirectly influence the migration and the transformation ability of elements from soils to plants. The aim of this study was to determine some selected physicochemical parameters (PCP) moisture contents (MC), moisture correction factors (MCF), pH, and electrical conductivity (EC) of soils to assess their effects on transfer of potentially toxic elements (PTE) As, Al, Cd, and Pb from soils to fruits. The PCP of soils were studied using soil slurries, the PTE in soils were determined by ICP and the transfer factors (TF) of PTE were calculated. The results showed that soils have low MC (10.50–11.25 %), moderately low EC ( $3.3x10^3-5.3x10^3 \ \mu$ S/cm) and slightly alkaline pH (7.45–8.66). Statistical test revealed that variation between PCP were statistically significant (P < 0.05). The results indicate that Pb and As (TF > 0.280) transfer more than Al and Cd (TF < 0.004), but the general ability of PTE to transfer from soils to plants were moderately low (TF < 1). The results of this study confirmed that the plants in the study areas were safe and could be used for human consumption without any health problems.

*Keywords:* Transfer factors, Physicochemical parameters, Potentially toxic elements, Soils, Fruits, ICP-method.

#### Introduction

Soil provides us all the basic nutrients that are considered the most important means for plants growth. 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, e.g. lead (Pb) and cadmium (Cd) in the environment can cause toxicity to both plants and animals [1, 2]. Arsenic (As) is a toxic element found as inorganic oxyanion arsenate As(V) and arsenite As(III) species [3]. Aluminium (Al) is essential in the trace level but access contents

may be leading to toxic effects for humans, flora and fauna [4].

The toxicity of PTE depends on the exposure route and the solubility of the PTE compounds. PTE tend to accumulate in the body, in tissues such as the brain, bones, kidney and liver. It has been found that the bioaccumulation of PTE in soils for long periods of time becomes toxic substance and of course will negatively affect the food chain and human health [5].

Soils are a heterogeneous mixture of different organisms, mineral and organomineral substances. It's considered one of nature's important and valuable resources to human life. All living organisms depend directly and/or indirectly on soils for their daily needs and > 95% of human foods are derived from the bounty of the earth. Developing healthy plans, pollution-free and productive soils are essential for the survival of humans and other organisms on this planet [6]. It acts as a filter, buffer and transformation system and thus protects the ecosystem from the harmful effects of various environmental pollutants [5]. It supports terrestrial life through many processes including biomass productivity, ecosystem restoration and resilience, water purification, pollutant detoxification and water cycling. Inherent soil physicochemical parameters (PCP) influence soil behaviors, therefore, the knowledge of soil properties is very important [4, 6, 7].

Plants are the primary and natural sources of food for all human beings on the earth. They contain large quantities of essential nutrients in very good proportions. Eating plants (e.g. fruits) on a regular basis is crucial in providing the overall healthpromoting nutrients to human organs. Furthermore, plants can be contaminated with toxic compounds from irrigation water and/or soil materials and/or through polluted air [8, 9].

Soils contaminations with PTE are now a growing concern due to food safety issues and potential health problems. Usually, the accumulation of PTE in plants occurs from various environmental resources such as water and/or air, but the pollution from the soils is considered as main one. Moreover, there are differences in the presence of PTE in plant depending on soil properties, irrigation water quality, prevailing climate and different growth conditions. Also, the accumulations of PTE in soils are associated with various human activities like the use of fertilizers, pesticides and other agrochemical substances [10-12].

Furthermore, the solubility of the PTE in soils depend on several parameters such as soil properties, soil composition, soil type, pH, temperature, nutrient balance, etc. PTE can also be transformed from soil through ion exchange, redox and precipitation reactions. In addition, the bioavailability of PTE in soil is a complex dynamic process and depends on many parameters such as biological, physical, chemical and environmental parameters [13]. It was found that the distribution of PTE in plants is heterogeneous and controlled by many parameters, the most important of which are genetic and/or environmental ones.

Plants can transfer PTE from soils through the roots as well as from the atmosphere through various plant organs like fruits, leaves and stems. The dynamics of absorption of PTE from soils by plants depend mainly on the interaction between plant tissues and element concentration in the soils. PTE pollution is released into the environment through many anthropogenic activities, like industrial manufacturing processes, domestic refuse, waste materials, waste water, etc.

Excess concentrations of PTE in soils have caused the disruption of natural terrestrial ecosystems. Likewise, different plants grown in the same soils may contain different levels of the same PTE [14, 15]. Since PTE easily accumulate in plants, soilplant-human-pathway has been considered as a major source of human exposure to macro and micronutrients. Some previous studies have indicated significant differences in the accumulation of PTE in plants [16–18].

The transport and accumulation of PTE in the soil plant chain (SPC) is part of the biochemical cycling of elements as these

elements flow from non-living to living parts of the biosphere. Each SPC contains specific parameters for transfer and bioaccumulation of PTE in plants, depending on many parameters of soil environments. One of the most important parameters is the soil pH, because it mainly affects the ionic form in which element is present in soils. While other parameters that control the mobility and availability of PTE in general include geochemical and climatic parameters in addition to biological parameters [16–18].

Moreover, soils electrolytes play an important role in the process of elements transfer and bioaccumulation of PTE in the SPC. The electrochemical properties of soils reflected through the temperature, the pH and the electrolyte concentrations. This influenced the migration and the transformation ability of PTE indirectly. These various parameters are usually studied using an indicator and/or transfer factor (TF) [16, 18].

Several studies have proven that PTE are environmental pollutants that threaten the human health and the natural environment. Some publications have indicated that the TF can be considered as a useful indicator of the transport capacities of potential PTE in soilplant-human-pathway. Also, TF have been widely used in the evolution of potential health risks of human exposure to PTE from soil. Moreover, the TF have been widely used in the knowledge and development of the potential health risks of elevation of PTE through soil-plant-human-pathway [16, 18].

High TF values (> 1) indicate a high transfer ability of PTE from soils to plants, while low values indicate a poor response. Thus, the prediction of PTE transfers by plants from a given medium must depend on several biotic and abiotic parameters that control their behavior in soils. The hazard to both the environment and human health from a given element is a function of its mobility and phyto-availability. Therefore, the behavioral properties of PTE in soils are a current issue in most recent environmental studies [16, 18].

In this context, some PCP of soil samples were examined in which fruit plants grow. These parameters include the pH, electrical conductivities (EC) and moisture contents (MC). These parameters affect the ionic form in which PTE are present in soils. Other parameters that may control mobility and the availability of PTE in general include geochemical, climatic, biological, as well as human factors. For these reasons, we have conducted a systematic survey of the environmental quality of soils and some plants in Wadi Turabah.

In order to understand the effects of some PCP (e.g. pH, EC and TF) on the transfer of PTE (e.g. Al, As, Cd and Pb) from soils by plants. In addition, for comparison purposes, MC and moisture correction factors (MCF) of soil samples under study were also estimated. Because all of these factors may affect, in one way or another, directly or indirectly the process of transferring these elements from the soils to plants.

# Materials and Methods Equipments and Reagents

A Perkin Elmer/Optima 2100 DV Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP–OES), USA, with chargecoupled device (CCD) detector was used for determination of PTE. The optimized operating conditions of ICP–method are shown in Table 1. Furthermore, CEM Corporation MARS 5 Digestion Microwave System (North Carolina, USA) was used to digest plant and soil samples. The MARS-5 heating program for digestion of plant and soil samples is also indicated in Table 2. An electric-oven (Gorkem, Turkey) was used to dry glassware and samples. Furthermore, some operating conditions of ICP-method, pH-meter, conductivity-meter, electric-oven and MARS-5 were set according to the manufacturer's instructions with minor modifications.

 Table 1. Optimized conditions for ICP-OES analysis

Method parameter	Selected value
Frequency (MHz)	40.68
RF-incident power <sup>a</sup> (W)	1600
Plasma Ar-gas flow rate (L/min)	15.0, Ar-gas
Nebulizer Ar-gas flow rate <sup>a</sup> (L/min)	0.60, Ar-gas
Auxiliary Ar-gas flow rate (L/min)	0.2, Ar-gas
Sample uptake flow rate <sup>a</sup> (mL/min)	1.0
Spectral emission lines <sup>a</sup> (nm): Al, As,	308.212, 188.979, 226.502,
Cd and Pb	and 220.353, respectively
<sup>a</sup> Optimized values	

Table 2. MARS-5 heating program for digestion method.

Method condition	Selected value
Pressure (psi)	800
Ventilation (min)	10
Ramp time (min)	25
Holding time (min)	10
Temperature <sup>a</sup> (°C)	220 and 250 for plant and soil samples respectively

<sup>a</sup>Optimized values

30% H<sub>2</sub>O<sub>2</sub>, 40% HF, 65% HNO<sub>3</sub> and 36% HCl (Merck, Germany) were used for samples preparations as received from the manufacturer. Also, high-purity grade(V) Atomic Spectroscopy Standard Solution that consist of Pb (2.0 mg/L), Cd (5.0 mg/L), As (10.0 mg/L) and Al (200.0 mg/L) was purchased from Perkin-Elmer. This solution was used to prepare standard solutions for calibration curves and also used to spike some soil and plant samples for recovery tests. Moreover, the purity of Ar and N<sub>2</sub> gases used in this study were > 99.99% (v/v). All glassware used in this study were soaked overnight in 10% HNO<sub>3</sub>, then rinsed several times and dried in an electric oven for 1 hour.

#### Study Area

Wadi Turabah (Fig. 1) is located at Turabah Province in the western part of (Makkah region). geographical The 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 1164 m (3819 Ft) above sea level. It extends over a length of 400 km with a hot climate. This area is considered one of the most fertile vallevs in the western region of the KSA. Soils of this area are sandy to fertile clay and seasonal plants such as watermelon and tomatoes grow in it, in addition to perennial plants such as palm dates. The sampling sites (read points) are shown in Fig. 1.

#### **Plants Sampling and Treatment**

The types of plants were chosen from the available varieties based on the high productivity and consumption by the population around the study areas. Sixty-three (63) plant samples were collected in clean polyethylene containers from six (6) points in Wadi Turabah. Samples include varieties such as tomatoes and watermelon and date palm. After collecting the outer surface of samples were first washed with DDW, then air dried and were kept in a refrigerator until treatment steps.

For drying process, samples of each type were first cut separately with a clean stainless-steel knife into small pieces in size (2-3 mm). Then mixed well and placed in an electric oven at 105 °C until constant weight. Three dried samples of each species were mixed, ground to a fine powder, and homogenized using a clean commercial kitchen grinder and stored in polyethylene containers (at -20 °C) until treatment processes.

0.5 g of each sample was accurately weighed into a PTFE digestion vessel and introduced into a Teflon digestion vessel of MARS-5. 2.0 and 4.0 mL of H<sub>2</sub>O<sub>2</sub> and HNO<sub>3</sub> were added to each sample, respectively. The contents were carefully shaken, then the digestion vessels were well closed and the digestion programs were followed. After digestion was completed, the contents of the vessels were quantitatively transferred into a 50 mL volumetric flask and diluted to the mark with DDW.

To ensure the robustness of the findings, sampling and the treatment steps were repeated three times (n=3) for each sample using the same steps. Furthermore, all statistical analysis were based on three measurements, i.e., n=3. This procedure was almost the same as to that reported in our last work with minor modifications. Furthermore, analytical blank solutions were prepared in the same way as the sample solutions to characterize the instrumental drift [19].

#### Soil Sampling and Treatment

Eighteen (18) soil samples were collected from six (6) sampling points in the same area where the plants under study were grown (Fig. 1). Soil texture in the study area was sandy clay soils with relatively low water and organic contents. Soil samples were taken from the surface (SS1, SS2 and SS3) points and depth (DS1, DS2 and DS3) points at 22.0 25.0 cm from the surface using a polyethylene spatula after the rainy season. Soil sampling points were selected based on an imaginary zigzag line pattern sampling method. Three samples from each point (500 g) were reduced to one representative sample by cone and quarter method [20]. Soil samples were ground using a mortar and pestle, passed through (63  $\mu$ m) nylon sieves, dried at 105 °C and cooled down in a desiccator. After cooling. samples were transferred to polyethylene containers and stored at -20 °C until needed for treatment. 0.25 g of each sample was accurately weighed into a PTFE digestion vessel and inserted directly into a Teflon digestion vessel of MARS-5. 1.0, 2.0, 3.0 and 9.0 mL of H<sub>2</sub>O<sub>2</sub>, HCl, HF and HNO<sub>3</sub> were added to each sample, respectively.



Figure 1. Map of Saudi Arabia showing the location of sampling sites (pink area), Wadi Turabah

Then the same treatment method that was done for the plant samples was followed till the end. This procedure was almost the same as that reported in our previous work with some modifications [21]. Moreover, several analytical blanks solutions were prepared in the same way as the samples for the same reasons as mentioned above [19].

# Measurement of Physicochemical Parameters of Soils

The study of PCP is important for soil management and plant growths. PCP of soil include MC (%), MCF, pH and EC. However, it would be valuable to discuss the potential impact of these parameters on the bioavailability and mobility of PTE in soil. Exploring how variations in these parameters may influence the transfer of PTE by plant would enhance the significance of our findings in this work.

#### **Moisture Content**

MC is defined as the ratio between the weight of total water content (moisture) in the wet soil and the weight of the dry soil after drying at 105 °C. Angle *et al.*, [22] reported that increasing MC of soils encouraged plants to produce more biomass and have a high potential to accumulate PTE.

In this work first crucibles were oven dried at 90 °C for 40 min and transferred to desiccators to cool down. After cooling, 5.0 g of air-dried from each soil samples was weighed in the crucible using an electronic analytical balance to record the initial weight. Then samples were dried in an electric oven at 105 °C till constant weight was achieved. Finally, the MC of the soil samples were calculated using equation (1) [23].

$$MC(\%) = \frac{W_{3} - W_{1}}{W_{2} - W_{1}} x100$$
(1)

Since  $W_1$ ,  $W_2$  and  $W_3$  represent the weight of crucible, weight of crucible + sample before drying and weight of crucible + sample after drying (at 105°C), respectively.

If the difference of MC (%) exceeds  $\pm 1\%$ , then MCF are required for this type of soils. The MCF of the soil samples were calculated using equation (2) [24].

$$MCF = \frac{100 - MC(\%)}{100}$$
(2)

For plant samples the crucibles were first oven dried at 90 °C for 40 min and then transferred to desiccator to cool down. After cooling, 5.0 g from each sample was weighed in the crucible using an electronic analytical balance to record the initial weight. Then samples were dried in an electric oven at 105 °C till constant weight. Finally, the MC (%) of the plant samples were calculated using equation (1) [24].

#### pH of Soil

Soils pH is a measure of hydrogen ions  $(H^+)$  activity in the soil solution, i.e., the acidity and the alkalinity of the soils [25]. The pH of soils has a major effect on metal dynamics because it controls adsorption and precipitation, which are the main mechanisms of metal retention in soils. As pH decreases, the solubility of cationic forms of element in the soil solution increases and therefore become more readily available to plants. The pH of soil in aqueous suspension was measured according to the procedure described by Feyisa et al., [26] with some modifications. 10 g of oven-dried soil sample was first weighed and transferred into 100 mL beaker to which 50 mL of DDW was added. This makes slurry made up of soil and water in a 1:5 ratio, then soil was allowed to settle down. Then the pH-meter was calibrated 25 °C with a buffer solution (pH=4.0, 7.0 and

9.0) according to FAO method. Finally, the glass rod of the pH-meter was placed in the prepared slurries and the pH-values were recorded.

# Electrical Conductivity of Soil

The EC is a measure of free ions (electrolytes) in solutions and its value depends on the dilution of the soil suspensions. Its value increases with the increases of ion numbers of the solution and vice versa. EC play an important role in the agricultural field due to the salinity of the land soils. The electrolytes of soils play an important role in the process of transporting minerals from soils to other plants organs [16].

The EC of soil samples were determined as described by Feyisa *et al.*, [26]. 10.0 g of oven-dried soil samples were weighed and transferred into 100 mL beaker to which 50 mL of DDW was added, this makes slurry made up of soils and water in a 1:5 ratio. Then the mixtures were stirred with a glass rod for 20 min and left to stand for 1 h. Furthermore, the soil was allowed to settle, and the EC-values were measured at 25 °C by inserting a conductivity-meter glass rod into the supernatant solutions.

#### **Transfer Factor Determination**

TF of PTE from soil- to plants have been studied using an indicator called TF. It reflects the ability of the plants to absorb and transfer of PTE deposits from the soils through the roots to other parts of the plant organs. It's also used as an important indicator for examining soils and/or plants quality and for evaluating health risks from contamination of plants and/or soils with PTE. It can be calculated as the ratio of the concentration (Conc.<sub>plants</sub>) of a particular element in the plants to the concentration (Conc.<sub>soils</sub>) of the same element in soils in which (land) plants were grown. Both (Conc.<sub>plants</sub>) and (Conc.<sub>soils</sub>) were represented in the same concentration units. The TF were calculated using equation (3) [16, 18, 27].

$$TFs = \frac{Conc_{plants}}{Conc_{soils}}$$
(3)

Since Conc.<sub>plants</sub> and Conc.<sub>soils</sub> represents the concentration of specific element in extracts of plant and soil (mg/kg) on dry weight basis, respectively. If the ratios are greater than one (> 1), this indicates that plants TF to soils elements are high. In this case the plants have great potential to accumulate the specific element. Moreover, if the ratios around one  $(\sim 1)$ , indicates that plants may not be affected by the specific element. Furthermore, if the ratios less than one (< 1), means plants may exclude the specific element from absorption. If certain plants have high TF (> 1), in that case plants can be used for elemental extraction and phyto-remediation. On the contrary, low values (< 1) indicate a poor response of plants to - transfer a particular element; -and suitable for the human consumption [18, 28].

# The Calibration Lines

Seven standard solutions were prepared by diluting a multi-element standard solution containing the elements under study. The blank solutions were prepared in the same as the standard solutions. Also, wav calibration curves were plotted for each element under study. Results were evaluated statistically by ANOVA-test and Student t-test (P=0.05), in addition to using both origin programs and Microsoft excel 2010. In this study all statistical calculations were based on three measurements, i.e., (n=3) [29].

#### **ICP-method Validation**

To evaluate the results of the analytical methods that used to analyze PTE in soil and

plant samples by the ICP-technique, some analytical figures of merits were calculated. These figures of merits include wavelengths (nm), linearity, squared correlation coefficient ( $R^2$ ), resolution, limit of detection (LOD) and limit of quantification (LOQ).

The wavelengths (nm) for each element were set on two (2) lines, primary (atomic) and secondary (ionic). The strategies and the criteria for choosing between atomic or ionic line were based on the sensitivity, spectral interferences and concentration range. Moreover, to measure the linearity of the calibration curves, the squared correlation coefficient was determined for each item under study. This was done by preparing a calibration curve using an un-weighted least squares linear regression line. To find out the accuracy of the applied analytical method, recovery values (%) were measured. This was done by spiking some plant and soil samples with the standard solutions and passing them through the same digestion steps. The squared correlation coefficient values were calculated using equation (4) [29].

$$r = \frac{n\sum(xy) - \sum x \sum y}{\sqrt{\left[n\sum(x^2) - (\sum x)^2\right]} \left[n\sum(y^2) - (\sum y)^2\right]}$$
(4)

The variable *r* represents correlation coefficient, n represents the total number of measurements (n=3),  $\Sigma x$ =total values of analyte concentration before spiking of samples with standard solutions,  $\Sigma y$ =total values of analyte concentration after spiking of samples with standard solutions,  $\Sigma xy$ =the sum of the product of x and y values,  $\Sigma x^2$ =sum of squares of the x values,  $\Sigma y^2$ =sum of squares of the y values.

The accuracy of the analytical method was estimated by calculating the relative standard deviation (RSD). The LOD and LOQ of the ICP-method were calculated for each element using equations (5) and (6), respectively [29].

$$LOD = \frac{3\sigma}{m} \tag{5}$$

$$LOD = \frac{10\sigma}{m} \tag{6}$$

The variable  $\sigma$  represent the standard deviation of the intensity of seven (7) blank solutions, while the variable m represents the slope of the calibration curve for each element under study.

#### **Determination of Potentially Toxic Elements**

All sample and standard solutions were analyzed three times (n=3) on a Perkin Elmer/Optima 2100 DV ICP–OES, USA, with CCD detector. The Cetac automatic sampler with 15 mL 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 all solutions. The concentrations of Al, As, Cd and Pb were determined in digested soil and plant samples using the optimized instrumental parameters.

#### Statistical analysis

The results were statistically evaluated by ANOVA test and Student t-test, (P= 0.05), in addition, Microsoft Excel and Origin software's were also used. The obtained concentrations were expressed as average value  $\pm$  confidence interval (at 95% confidence interval). All statistical analysis was based upon triplicate measurements.

# **Results and Discussion** *ICP-OES-parameters Optimization*

The emission intensity of ICP-OES is mostly affected by radio frequency (RF) incident power, Ar-gas nebulizer flow rate, sample transfer flow rate and the spectral emission line. Whereas plasma and auxiliary Ar-gas flow rate and frequency have relatively small effects on sensitivity and are adjusted to accommodate memory effects due to a particular sample type such as organic component and/or total dissolved solids. The RF-incident power was studied in the range 1400–1800 W. The results indicate that sensitivity and linearity were better at 1600 W for nearly almost all desired elements (Table 1).

Also, the effect of nebulizer Ar-gas flow rate was studied between 0.40–0.80 L/min. A maximum intensity of 0.60 L/min was observed for almost all desired elements, thus a flow rate of 0.60 L/min of nebulizer Argas was adopted throughout this study (Table 1).

Furthermore, the sample uptake flow rate was investigated at three levels: 1.0, 2.0 and 3.0 mL/min. It was found that the emission intensities of As. Cd. and Pb were high at 1.0 mL/min, while of Al was slightly high at 2.0 mL/min. Therefore, sample uptake flow rate of 1.0 mL/min was chosen for this provides study, which low sample consumption sensitivity and sufficient (Table 1).

The radiations from the emissions of other elements overlap with the spectral emission line of desired element and cause spectral interferences. This can be minimized using an alternative spectral emission lines. In this context all studied elements were measured in two different spectral emission lines, ionic and atomic line. These lines include 308.212 and 237.313, 188.979 and 234.980, 214.440 and 226.502, 220.353 and 217.000 nm for Al, As, Cd and Pb, respectively. The strategies and the criteria for choosing between them were based on the sensitivity. spectral interferences and

concentration range of each element [30]. The specific selected lines (nm) for the desired elements that provide better sensitivity and less spectral interferences are indicated in Table 1.

Although, ICP-techniques is one of the most sensitive and selective analytical methods, it often suffers from matrix effect problems. In our study these problems were solved and minimized as much as possible by sample dilution processes.

# Microwave Parameters Optimization

Since the efficacy of sample digestion depends on the sample matrix, so it's important to optimize MARS-5 conditions. MARS-5 temperature and acid/oxidant digestion mixture further effects sample digestion. While, pressure, holding, ramp, and the ventilation time have relatively small effects on samples digestibility.

According to preliminary experiments in addition to our previous work, the temperature was set between 210-260 °C [19]. A clear solution was obtained at 220 and 250 °C for plant and soil samples, respectively. Therefore, oven temperature at 220 and 250 °C were used in this study. Furthermore. the acid/oxidant mixture (H<sub>2</sub>O<sub>2</sub>/HNO<sub>3</sub>) has been studied in a ratio of 1:1, 1:2, 1:3, 1:4 and 1:5, a clear solution was observed in a ratio of 1:2. Thus, a ratio of 1:2 was used to digest plant samples throughout this work. While an acid/oxidizing mixture (H<sub>2</sub>O<sub>2</sub>:HCl:HF:HNO<sub>3</sub>) in a ratio of 1:1:2:7, 1:2:4:8, 1:2:3:9, 1:3:5:9 and 1:4:6:10 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 soil The optimal in this study. samples values of MARS-5 parameters are shown in Table 2.

РТЕ	R <sup>2</sup>	Slope (m)	Intercept (b)	RSD (%) <sup>a</sup>	Recoveries (%)	LOD (mg/kg)	LOQ (mg/kg)
Al	0.9993	1.8594	0.0783	3.16	106±3	0.0557	0.175
As	0.9998	1.3999	0.0001	1.02	102±5	0.0054	0.017
Cd	0.9990	3.6714	0.0714	2.84	104±4	0.0007	0.019
Pb	0.9998	1.3996	0.0081	2.98	98±4	0.0062	0.085

*Table 3.* The analytical figure of merits for the determination of PTE.

<sup>a</sup>RSD (%) are expressed as mean  $\pm$  SD; slope (m), y-intercept (b) and squared correlation coefficient (R<sup>2</sup>) were calculated using the equation:- y = mx + b

#### The Analytical Figures of Merits

The linearity of the method was investigated using the selected analytical line determined at five (5) concentrations in the range of 0.04-100 mg/L (Table 3). Those were satisfactory for all desired elements with R<sup>2</sup> higher than 0.9990 in linear regression curves. This confirms the linearity of the used analytical technique according to the standards set by AOAC [31].

The accuracy of the analytical method was determined as recovery values (%), and it was found to be within the acceptable range for all desired elements  $100\pm5$  (Table 3). This indicates that there are no significant gains or losses for desired elements using the developed analytical technique.

addition, the precision of In ICP-method was calculated as RSD of five independent replicates for each sample and it was found to be < 3.17% (Table 3). This value confirms the good precision of the used analytical method. The LOD (mg/kg) of the desired elements were ranged between 0.0007-0.0557 mg/kg for Cd and Al, respectively; while LOQ (mg/kg) were ranged between 0.017 mg/kg for As and 0.175 mg/Kg for Al (Table 3). The obtained values of LOD and LOQ clearly demonstrated the high sensitivity and linear range of the ICP-method.

# Measurements of Physicochemical Parameters

Measurement of PCP (e.g. MC, MCF, pH, EC) is very important for plants growth and soils management. Also, the physicochemical study of parameters is vital because it explains the conditions that favor transmission of PTE form soils to plants [32]. The results in Table 4 show that MC and MCF values of the studied soil samples were ranged between 10.50-11.25% and 0.888-0.895, respectively. The statistical test revealed not significantly difference with a confidence level of 95% (P< 0.05), between the values of MC and that of MCF in different varieties of soil samples under study.

Soils pH is a measure of H<sup>+</sup> activity in the soil solutions and it expresses the acidity and alkalinity of the soils [32]. From the three repeated measurements (n=3) of 1:5 soils to water ratio (soil slurries), the pH values were ranged between 7.45–8.66 (Table 4). These values indicated that soils were slightly alkaline and it considered as within the permissible limits (4.0–8.5) set by FAO [24]. The pH value for normal soil is 5.5-7.5; pH of soils below this range can cause low availability of some elements needed by the soils. This also shows the soil samples are within the range for normal soils pH [32].

Addis and Abebaw [25] and Uquetan, *et al.*, [33], reported that the

maximum availability of essential nutrients required for plants growth is greatest at a pH value between 6.5–7.5. Based on the pH values of soils in the area under study, it was observed that, it can increase the ability to absorb nutrients, and this will enhance plants growth. Moreover, Odoemelam and Ajunwa [34] showed that the application of bio-solids like animal manure and compost on acidic soils this significantly increases soils fertility. Statistical test of significance using ANOVAtest revealed no significant differences with a confidence level of 95%, between the pH values in soil samples under study.

The EC is a measure of free ions in solutions, its value depends on the dilution of the soil suspensions. It increases with the increases the number of ions in the solution and vice versa. In this study, measured EC of soil samples were ranged between  $3.3 \times 10^3 - 5.3 \times 10^3$  µS/cm (Table 4). These values indicate the relative water-soluble salt content of soils. Horneck *et al.*, [35] reported that soils EC between  $0.0 - 1.0 \times 10^3$ 

Table 4. Results of physicochemical parameters of soils.

 $\mu$ S/cm is while good, between  $1.0x10^3 - 2.0x10^3$ µS/cm is poor seed germination. Moreover, they reported that soils EC between  $2.0 \times 10^3 - 4.0 \times 10^3$  µS/cm is harm to some plants and  $> 4.0 \times 10^3 \,\mu\text{S/cm}$  is harm to all plants. Therefore, based on this classification soil samples under study were ranged between moderate to harmful.

Abdulhamid *et al.*, [32] classified EC of soils as: non saline < 2; moderately saline 2–8; very saline 8–16; extremely saline >16. Based on this classification, the EC results for this study may be classified as extremely saline. The difference in the EC values could be attributed to the differences in the soluble salt contents in soils. Table 5 reported some studies of some PCP of soils for comparison purposes. Statistical test by ANOVA-test revealed that no significant differences with a confidence level of 95%, between the values of EC in soil samples obtained from study areas.

Parameters	PCP of soils						Level
	SS1	SS2	SS3	DS1	DS2	DS3	-
MC (%)	11.11	11.25	10.50	10.70	10.89	11.01	10.50-11.25
MCF	0.889	0.888	0.895	0.893	0.891	0.890	0.888-0.895
pН	7.57	7.45	8.66	7.96	8.31	7.94	7.45-8.66
EC ( $\mu$ S/cm)	5.0x10 <sup>3</sup>	5.3x10 <sup>3</sup>	3.3x10 <sup>3</sup>	$3.4x10^{3}$	3.9x10 <sup>3</sup>	$4.7 \text{x} 10^3$	$3.3 \times 10^3 - 5.3 \times 10^3$

Table 5. Comparison of some physicochemical parameters of soils in current study with other values reported in literature.

PCP of soils			Gaussian	D-f
pН	EC (µS/cm)	MC (%)	Country	Keterence
7.66-9.48	103.7-4140.0	-	India	[6]
7.87-8.23	174-319	-	Ethiopia	[9]
6.8-6.95	18-21	35-56	Nigeria	[23]
6.53-7.64	0.09-0.34	7.35-11.01	Ethiopia	[25]
5.77-7.70	17-37	-	Nigeria	[32]
6.45-6.66	630-890	10.50-11.25	Ethiopia	[36]
7.45-8.66	$3.3x10^3 - 5.3x10^3$	10.50-11.25	KSA	Present study

# Potentially Toxic Elements in Soils and Plants

The method was used to identify PTE in samples of soils and plants in which they were grown. The concentrations (mean, sample by dry weight) of PTE in soil samples were shown in Table 6. Also, the same method was used to identify PTE in three varieties of the most commonly plants in Turabah governorate and other regions in KSA.

The investigation of PTE in the soil samples under study (Table 6) showed high content of Al in almost all samples (50.22-104.2 mg/kg). Moreover, Cd was not detected (ND) in all soil samples under study, because its concentration was lower than the LOD of the ICP-method. Unexpectedly, As and Pb were found in all studied soil samples but with very low mean concentrations (0.039)and 0.089 mg/kg, respectively). Furthermore, the results indicated that PTE accumulated more on SS than on DS. The results in Table 6 showed that some statistically significant differences were observed regarding PTE concentrations in the studied soil samples (Fig. 2). The differences in concentrations were significant at confidence level of 95%. The order of concentration of PTE in the soil samples under study was as follows: - Al > As> Pb > Cd (Table 6 and Fig. 2).

Table 6. Potentially toxic elements contents in studied soil samples.

Sample	PTE (	Mean Conc.			
	Al	As	Cd	Pb	(mg/kg)
SS1	80.54	0.132	ND	0.043	20.16
SS2 SS3 DS1	104.2 50.22 60.14	0.119 0.028 0.084	ND ND ND	0.034 0.079 0.037	26.09 12.58 15.07
DS2 DS3	51.38 76.98	0.067 0.105	ND ND	0.022 0.018	12.87 19.28
Mean Conc. (mg/Kg)	70.58	0.089	NC	0.039	17.68

ND: not detected (below LOD of the ICP); NC: not calculated (below LOD of the ICP)



Figure 2. Potentially toxic elements contents in studied soil samples

Furthermore. the determined concentrations (mean, sample by dry weight) of PTE in plant samples are shown in Table 7. The MC of a food sample is the total water component and it used to determine the quality of a food sample. The values of MC of the studied plant samples are shown in Table 7. The differences in MCF values of tomatoes and watermelon were not significant because both fruits were still fresh when collected from the lands. MC for date palms was significant due to their semi-dry moisture (rutab) when collected from the lands. It was observed that higher the MC value, the more vulnerable the fruit to microbial attack and vice versa.

The results (Table 7) indicated that elevated Al levels were found in watermelon with mean concentration of 0.187 mg/kg. While Al was ND in tomatoes because its concentration is lower than the LOD of the ICP-method. Unexpected results were found that As, Cd and Pb in almost all types of plants under study, but at very low mean concentrations (0.025, 0.032, and 0.043 mg/kg, respectively). Moreover, the high mean concentrations of PTE were recorded in watermelon (0.149 mg/kg), while the low concentration was recorded in tomatoes (0.021 mg/kg).

Sample name	MC (%)		Mean Conc.			
(English / Scientific)	MC (70)	Al	As	Cd	Pb	(mg/kg)
Tomatoes (Solanum lycopersicum L)	94.5	ND	ND	0.033	0.049	0.021
Date palm <sup>a</sup> ( <i>Phoenix dactylifera L</i> )	21.8	0.118	0.033	0.033	ND	0.046
Watermelon (Citrullus lanatus L)	92.7	0.444	0.042	0.030	0.080	0.149
Mean Conc. (mg/kg)	-	0.187	0.025	0.032	0.043	0.072

Table 7. Potentially toxic elements and moisture contents in studied plant samples.

<sup>a</sup>Wet stage of fruit; ND: not detected (below the LOD of the ICP)

Moreover, the present results (Table 7) showed that significant differences were observed regarding PTE concentrations in the different studied plant samples (Fig. 3). The differences were significant for different samples with a confidence level of 95%.

The order of concentrations of PTE in the three plant varieties were increases in the order:- Al > Pb > Cd > As (Table 7 and Fig. 3). Furthermore, when plants grows on the same soils, the accumulation of PTE in different and were decreases in the order: tomatoes < date palm < watermelon (Table 7 and Fig. 3). However, generally, we can say that the concentration of the studied PTE in plant samples from Wadi Turabah were lower than the maximum permissible concentrations in plants that were given by WHO and FAO [8, 9, 37].



Figure 3. Potentially toxic elements contents in studied plant samples

#### **Comparison of PTE Contents**

Fig. 4 show the relationship between the concentration of PTE contents in plant soil samples. The differences in and PTE concentrations in soil samples may be related to differences in soil textures, soil properties, soil structures and chemical and mineral composition of soils. While the differences in the concentrations of PTE in the plant samples may be due to plants physiology and plant species. Also, it may relate to metal speciation or due to differences in their concentrations in soil. It may also be from the nature and formation of roots, osmotic pressure, and other physical and chemical properties of soil. In addition, the morphology of plants in general affects the deposition of dust on them and thus leads to different occurrence of PTE on different parts of plants.

Furthermore, metal speciation and nutrient availability could be explored to elucidate the underlying mechanisms of PTE transfer bioaccumulation. and Therefore. it can be said that the bioaccumulation mechanisms of PTE in plants are a combined and affects the transfer of PTE by roots from the soil solutions.

The results (Tables 6 and 7 and Fig. 4) indicated that the concentration of PTE is

relatively high in soil samples compared to plant samples. Dilek and Ahmet [38], reported that the level of PTE in plants were generally lower than in soil samples. Moreover, high levels of PTE in soil samples do not always indicate similar high concentrations in plant samples.



*Figure 4.* Relationship between potentially toxic elements concentration in plant and soil samples

# TF of PTE from Soils to Plants

The ability of a particular element to migrate and pass from soils to plants was referred to as TF for that element. It was calculated for the level of transfer and translocations from soils by plants. Its value reflects the actual ability of plants to absorb and transport a particular element from soils [16, 18, 27, 38]. A high value of TF indicates that plants can absorb and accumulate macro and micronutrients. and this may pose a potential health risk to the consumers of those plants [27]. While a low value indicates a weak response of plants to absorb and accumulate macro and micronutrients. Our finding indicates that moderately low TF (< 1), so that plants in study areas can be used for human consumption without any health problems [15]. Thus, the soil-to-plant transfer of PTE might not pose а potential health risk to the local residents. The TF values of PTE from soils to plants (mg/kg) are shown in Table 8, Fig. 5 and 6.

Table 8. Transfer factors of potentially toxic elements from soils to plants.

Sample name		Mean			
(English / Scientific)	Al	As	Cd	Pb	values
Tomatoes (Solanum lycopersicum L)	NC	NC	NC	1.103	0.001 (< 1)
Date palm <sup>a</sup> ( <i>Phoenix dactylifera L</i> )	0.002	0.371	NC	NC	0.003 (< 1)
Watermelon (Citrullus lanatus L)	0.006	0.472	NC	2.051	0.008 (< 1)
Mean values	0.003 (< 1)	0.281 (< 1)	NC	1.102 (>1)	0.004 (< 1)

<sup>a</sup>Wet stage of fruit; NC: not calculated (below the LOD of the ICP)



Figure 5. Transfer factors of potentially toxic elements from soils to plants



Figure 6. Transfer factors of potentially toxic elements by plants from soils

The results presented in Table 8 show that Pb has the high mean TF (1.102, i.e., > 1), As has moderate mean TF (0.281, i.e., < 1). While, Al and Cd have the low mean TF (0.003, i.e., < 1 and NC, respectively). This means that the roots of plants can easily absorb Pb from the soil and accumulate it in various plant organs like fruits. On the other hand, it was observed that the roots of plants do not have sufficient ability to easily absorb Cd from soils and accumulate them in plant organs [16]. The high TF values of Pb (> 1) may be due to its natural occurrence in soils and their greater mobility compared to other PTE in soils (Fig. 5).

The results in Table 8 also support that As accumulation is relatively less than that of Pb in plants (Fig. 5). It was also observed that watermelon shows a high affinity towards Pb than other PTE (Fig. 6). Furthermore, the present result agrees with the investigation that was made by Yeasmin *et al.*, [16] and Zhuang *et al.*, [39]. They observed and concluded that the bioaccumulation parameters for PTE were significantly high for leafy than non-leafy plants. Form the above-mentioned reasons; plants (fruits) must be washed well as much as possible before consuming. This will help to remove dirt, dust, remaining fertilizers, pesticides, PTE, etc. [31].

#### Influence of PCP for PTE Transfer

In the current study (Tables 6 and 7), high PTE contents were found in SS2 and watermelon samples with a mean values of 26.09 and 0.149 mg/kg, respectively. It was observed that SS2 had a high mean value of PTE (26.09 mg/kg), MC (11.25%) and EC  $(5.3 \times 10^3 \text{ } \mu\text{S/cm})$ . Also it had a low mean value for both MCF (0.888) and pH (7.45). On contrary, low mean values of PTE were found in SS3 and tomatoes samples with mean values of 12.58 and 0.021 mg/kg, respectively. Furthermore, SS3 was observed to have a low mean value of PTE (12.58 mg/kg), MC (10.50%), EC ( $3.3x10^3 \mu$ S/cm) and high mean values of MCF (0.895) and pH (9.66). The pH of most of the soil samples were found to be slightly alkaline (pH > 7). EC were high near surface area indicating the effect on soluble salts content of the soils.

In summary, most of the soil samples under study have low MC and EC as well as moderately high pH values. The results of this study confirm that plants generally have weak responses to transfer most of PTE from the soils (i.e., TF < 1). Therefore, plants of Wadi Turabah can be used for human consumption without any health problems. In contrary, if a particular plants have a high TF; it can therefore be used as a biomarker for contamination with certain elements [17].

#### Conclusion

The physicochemical study of certain parameters is very important for plants growth and soils managements. This study gives information about the pH, EC and MC of the soils and the PTE ability to transfer from soils to plants. Regarding to the ability of elements to pass from soils to plants, studied plants have a moderately low ability to absorb and accumulate PTE in their different organs (e.g. fruits). We can conclude that the PTE contents in studied samples were almost all within the safe limits prescribed by the FAO/WHO and EU standards except for A1 [32, 40]. The high level of Al may constitute health hazards due to its toxicity; therefore more attention should be given especially to children because of their sensitivity to PTE. The PCP of studied soil samples in area under study show significant variations. Therefore routine PCP and PTE analysis of soils should be carried out in order to maintain the quality of plans that will grow in Wadi Turabah.

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#### **Conflict of Interest**

The author of this paper declares that he has no conflicts of interest.

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