Trace metals assessment in agricultural soil and irrigation water at Hail region Saudi Arabia

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Abstract

The suitability of agricultural soil and irrigation water depends on the presence of trace metals; the aim of the present work is to assessment of the trace metals at Hail region using analytical techniques. The metal contaminations levels were determined using ICP-MS and flame photometer. The result obtained were compared to the standard samples suitable for agricultural and it was in the suitable range. The geo-accumulation (I-geo), single pollution, Nemerow pollution indices showed that the Se pollution intensity was significant for agricultural soils. I-geo values revealed no real sign of contamination with almost all the samples, reflecting a lack of contamination for all elements except Zn. While the enrichment factor (EF) for Fe was less than 2 suggested that the elements come entirely from crustal materials or natural processes. The study showed considerable variation in the levels of the analyzed elements in the soil samples. The total metal concentrations in the soil samples ordered as follows: Na > K > Fe > Mn > Zn > Ba > Cr > Ni > Cu > Pb > Cd > As.

Keywords: Contamination assessment; Water; Agricultural soil; ICP-MS; Trace metals; Saudi Arabia; Hail region

1. Introduction

The suitability of water and soil for agriculture depend on the presence and concentrations of some elements, specially the heavy metals. In the last years and due to increment of the human activities the water pollution by heavy metals increased rapidly and the estimation of this metals periodically is so important process to understand the suitability of the irrigation water and soil for the agriculture. Heavy metals are widespread pollutants of great environmental concern as they are non degradable, toxic, and persistent [1-3]. Heavy metals and some trace elements are biologically toxic and can affect the health of human being owing to their accumulation and persistence in the compartments of the food chain. Heavy metals become toxic at a certain concentrations and when they are not metabolized in the body and accumulate in the soft tissues [4-5]. The area of the research in the aquatic chemistry of some trace elements is sovibrent areas and considered as a very needing research area with a wide spectrum of aspects and considerations to be studied for the soil and water. The determination of trace elements in water and soil is of widespread and great importance. Trace elements can be categorized as (1) essential to human life (chromium, copper, iodine, molybdenum, selenium, and zinc), (2, 3) probably essential (boron, manganese, nickel, silicon, and vanadium), and potentially toxic, some of which possibly have essential functions (aluminum, arsenic, cadmium, fluoride, lead, lithium, mercury, and tin) [3]. Groundwater is one of the most important natural resources for domestic, agricultural and industrial uses in an arid country like Saudi Arabia.

The previous study on the Soil and water samples at Hail Region KSA, was conducted at 2016; from about 5 years ago and not covered all Hail areas. During that period of time the concentrations of trace elements have been changed so the periodic estimation of the trace metals is tremendous.
Analytical and electroanalytical techniques are highly effectiveness for the trace elements deriminations [13-22]. From the most popular analytica techniques are Atomic absorption spectroscopy, AAS, gravemetric, complexmetric, ICP-MS, and UV- Spectroscopy 13-22]. The most popular electrochemical method for determination of trace elements in water samples, are the potentiometry and voltammetry. This methods is very sensitive for many elemental analysis, and can be used for simultinuous determination at low cost. In particular, it is favorable for the analysis of many elements like cadmium, copper, lead and zinc [7-9]. So, the aim of the present research is to investigate the distribution of some elements in the irrigation water and agricultural soil at Hail region to assess the element contamination levels and to reach the suitability of the water and soil for agriculture by through comparison models studies and using analytical techniques. The analytical techniques which will be used in this study are Atomic absorption spectroscopy, AAS, and ICP-MS. The results were compared According to soil quality guidelines. Both geo-accumulation (I-geo), single pollution, and Nemerow pollution will be used to gain information about the sources of metal pollutants and to assess the metal pollution status. All the data obtained from the used different techniques were compared and discuss to in order to determine the suitability of the water and soil for agriculture at Hail Region KSA.

2. Material and methods

2.1 The Area of the Study

This study was conducted during 2020 in agricultural areas at Hail region, and its Villages [23]. The average annual rainfall in study location is about 10.16 cm without any, or with a negligible amount, of rains in the summer season [24].

2.2 Water sample collection and analysis

Ground water samples used for irrigation were collected and preserved according to the operating procedure for groundwater sampling [23-25]. A total of fifty samples were brought from several farms within the Hail area. Well Tight-capped high quality polyethylene terephthalate bottles were used for sample storage. Before use, the bottles were washed by distilled deionized water and rinsed overnight in 10% (v/v) nitric acid. Samples were filtered through the Whatmann filter papers number 42. To prevent precipitation of metals and biological growth, few drops of concentrated nitric acid were added to samples to obtain pH nearby 2 [26,27]. Thereafter, samples were immediately transported to the laboratory in iceboxes and stored at 4 °C up to analysis. The elements were measured using Thermo Scientific iCAPQ ICP-MS with CETAC ASX-520 Autosampler). The precision of the water method analysis for the multi-element determination was evaluated by using triplicate readings for each analysis, and the mean was calculated with relative standard deviations less than 4%.

2.3 Soil samples collection and analysis

A total of 50 soil samples were collected from agricultural farms situated along the main highways in the Hail region and her Villages during 2018. The samples were collected from the upper 10 cm sections. After grinding and sieving through 2 mm mesh, 500 mg were digested according to [26, 27]. The elements were measured using an ICP-MS: With Auto Sampler ICAP Q, CETAC ASX-520, Thermo scientific USA. The precision of the soil method analysis for the multi-element determination was evaluated by using triplicate readings for each analysis, and the mean was calculated with relative standard deviations less than 4%.

2.4 Contamination level of elements

I-geo, pollution load index (PLI), and enrichment factors were used to gain information about the sources of metal pollutants and to assess the metal pollution status.

2.4.1 Pollution Load Index

PLI was evaluated as follows equation (1) [25-28];

\[
PLI = \left(\frac{P_{i1} \times P_{i2} \times P_{i3} \times ... \times P_{in}}{1}\right)^{1/n}
\]  

(1)

Where \(n\) is the number of elements, and \(P_i\) is the single pollution index by element \(i\), it is the ratio between the element level \((C_i)\) in soil samples and its background concentration \((S_i)\) and given by the following equation (2):

\[
P_i = \frac{C_i}{S_i}
\]  

(2)

Where PLI value >1 would indicate a contaminated site while PLI value <1 indicates no contamination.
2.4.2 Geo-accumulation index

$I_{geo}$ was computed as follows, equation (3) [28,29].

$$I_{geo} = \log_2 \left( \frac{C_n}{1.5B_n} \right)$$  \hspace{1cm} (3)

Where $C_n$ is the total metal concentration in the soil sample; $B_n$ is the metal background value, and the value 1.5 represent the factor for background matrix correction. $I_{geo}$ consists of seven classes as shown in Table 1. The concentrations [µg/g] of Zn (200), Cu (63), Pb (70), Ni (45), Co (40), Cr (64), Se (1) and Cd (1.4) in the Canadian soil quality guidelines [21], were used as background.

Table 1 Descriptive classes for $I_{geo}$ values

| $I_{geo}$ Class | 0  | 1   | 2   | 3   | 4   | 5   | 6   |
|-----------------|----|-----|-----|-----|-----|-----|-----|
| $I_{geo}$      | 0< | $I_{geo}$≤1 | 1< | $I_{geo}$≤2 | 2< | $I_{geo}$≤3 | 3< | $I_{geo}$≤4 | 4< | $I_{geo}$≤5 | $I_{geo}$>5 |
| Sediment quality | Unpolluted | Unpolluted to moderately polluted | Moderately polluted | Moderately to heavily polluted | Heavily polluted | Heavily to extremely polluted | Extremely polluted |

2.4.3 Nemerow pollution index

The Nemerow integrated pollution index $P$ considers the average values of all studied elements in addition to the maximum value of $P_i$, where $P_{ave}$ and $P_{max}$ represent the average and maximum of the pollution indices for each element, respectively [29]. The following equation determines $P$: Equation (3) [22].

$$P = \sqrt{\frac{P_{max}^2 + P_{ave}^2}{2}}$$  \hspace{1cm} (4)

2.4.4 Enrichment Factor

The EF of a single trace element in the soils was calculated as follows equation (5) [30].

$$EF = \frac{(M/Al)_{sample}}{(M/Al)_{background}}$$  \hspace{1cm} (5)

Al was used as a conservative tracer to differentiate natural from anthropogenic components. $(M/Al)_{sample}$ is the ratio of metal, and Al concentration in the sample in the examined environment and $(M/Al)_{background}$ is the ratio of metal and Al concentration of the background [24]. The background concentrations of Fe, Mn, Zn, Cu, Ni, Cr, Pb, Cd, Co and Se in the Upper Continental Crust obtained from TAYLOR and MCLENNAN [31] were used. EF values were classified as EF<2, clean-light pollution; 2 ≤ EF < 5, moderate pollution; 5 ≤ EF < 20, significant pollution; 20 ≤ EF < 40, strong pollution; EF ≥ 40, extreme pollution. Data of water and soil samples were examined for significant differences for all studied elements fractions among different locations by ANOVA test.

3. Results and discussion

3.1 Metals Concentrations in Hail irrigation water

The concentrations of trace elements in the hail irrigation water was measured by ICP-MS analytical techniques for all elements except Na and K which were measured using the flame photometer all concentrations are mentioned in µg/L. the data obtained were summarized in table 2. As show in table 2 that: the concentrations [µg/L] of elements in the ground water used for irrigation in Hail area. No significant differences ($P > 0.05$) in the water trace elements concentration were observed between the studied sites along Hail region. The perusal water data revealed that, the trend of elements according to mean concentration in the samples was: Na > K > Mn > Ba > Fe > Zn > Pb > Cr > Ni > Cu > Cd > As. The variation in trace elements concentration is controlled by the variation in local and regional geology, water/rock interactions, dilution due to precipitation [2].
were exist in the trace concentrations. Divalent element y at plentiful levels, thus are rarely affected by anthropogenic inputs. For agricultural applications, metals vary in the range of Cr > Ni > Cu > Pb > Cd > As.

The variation in trace elements concentration in Hail region may be due to irrigation of land by fertilizers and other agronomic practices containing metals. Across the investigated samples, wide elements concentration ranges have been recorded in Table 3. No significant differences (P > 0.05) in the soil trace elements concentration were observed between the studied sites along Hail region. Soil contamination with toxic and trace elements due to point sources or parent materials often occurs and is easy to identify. The use of elements-enriched chemicals, fertilizers, and organic amendments such as sewage sludge as well as wastewater may cause contamination at a large scale [32]. The higher concentration of Na and K is normal which result from the nature of soil and the decay of the plants tissue, papers, and routes. Fe is the fourth most abundant element in the Earth’s crust. It is the most predominant among studied elements in the Hail region and varied in the range of 8.37-29.89 mg/g. It is considered an essential metal to controlling the behavior of several micronutrients in the soil, but it may cause severe problems if found in high levels. Various reports indicating the high application of Mn in agriculture are available [35]. Although Zn is an essential trace element, high levels can cause harmful health effects. Zn varied in the range of 43.29-1293 μg/g, where 70% of samples were estimated to be more than the maximum permissible level cited by CCME, indicating that there is relatively Zn pollution and relating to the application of Zn fertilizer. Barium (Ba) concentrations range was 21.21 μg/L in the irrigation water samples. The Ba concentrations higher than the CCME limit (100 μg/L) for irrigation water. The US Environmental Protection Agency found that acute exposure to Ba at above the maximum contaminant level (2 mg/L) can potentially cause gastrointestinal disturbances and muscular weakness. Long-term exposure to Ba at can also potentially cause hypertension. There is no evidence that lifetime exposure to Ba in drinking water has the potential to cause cancer [33]. Other elements from Cr to As (Cr > Ni > Cu > Pb > Cd > As) were exist in the trace concentrations. The mean values of Cr, Ni, Cu, Pb, Cd, and As did not exceed the Canadian soil guidelines, which mean that the soil is not contaminated. Zn were present in high levels and had a significant contamination level compared to other elements.

### Table 2 Summary of elements concentrations µg /L in Hail irrigation water

| Variable | Max   | Min | Median | Mean   | SD    | CCME (2007) |
|----------|-------|-----|--------|--------|-------|-------------|
| Na       | 3670  | 16  | 418    | 819.057| 1055.701| -           |
| K        | 68.1  | 1.4 | 7.5    | 11.7532| 15.61767| -           |
| As       | 0.001 | 0.001| 0.001  | 0.001  | 4.44*10^-19| 100         |
| Cd       | 0.001 | 0.001| 0.001  | 0.001  | 4.44*10^-19| 5.1         |
| Pb       | 0.036 | 0.001| 0.001  | 0.001  | 0.007638| 200         |
| Cr       | 0.0138| 0.001| 0.001  | 0.001  | 0.004258| 8           |
| Ni       | 0.001 | 0.001| 0.001  | 0.001  | 4.44*10^-19| 200         |
| Fe       | 0.07941| 0.0057| 0.00314| 0.00997| 0.018668| 5000        |
| Mn       | 13.164| 0.00501| 0.001  | 0.628115| 2.872332| 200         |
| Ba       | 0.0819| 0.00504| 0.0319  | 0.034799| 0.019752| 100         |
| Cu       | 0.001 | 0.001| 0.001  | 0.001  | 4.44*10^-19| -           |
| Zn       | 0.04415| 0.0058| 0.001  | 0.005285| 0.010925| -           |

### 3.2 Metals Concentrations in Hail soil

The concentrations of the trace metals in the agricultural soil were measured by ICP-MS analytical techniques for all elements except Na and K which were measured using the flame photometer all concentrations are mentioned in µg /L. The data obtained were summarized in table 3. As show in table 3 that: the trend of elements according to mean concentration was: Na > K > Fe > Mn > Zn > Ba > Cr > Ni > Cu > Pb > Cd > As. The variation in trace elements concentration in Hail region may be due to irrigation of land by fertilizers and other agronomic practices containing metals. Across the investigated samples, wide elements concentration ranges have been recorded in Table 3. No significant differences (P > 0.05) in the soil trace elements concentration were observed between the studied sites along Hail region. Soil contamination with toxic and trace elements due to point sources or parent materials often occurs and is easy to identify. The use of elements-enriched chemicals, fertilizers, and organic amendments such as sewage sludge as well as wastewater may cause contamination at a large scale [32]. The higher concentration of Na and K is normal which result from the nature of soil and the decay of the plants tissue, papers, and routes. Fe is the fourth most abundant element in the Earth’s crust. It is the most predominant among studied elements in the Hail region and varied in the range of 8.37-29.89 mg/g. The Hail soil had distinctive red color owing to the occurrence of iron oxides [33], so the Fe concentrations of a soil are region specific and can vary considerably locally due to soil types. Various results revealed the very high levels of Fe in soils and concluded their carcinogenic/mutagenic effects on the living being’s health [34]. Fe and Mn occur naturally at plentiful levels, thus are rarely affected by anthropogenic inputs. For agricultural considerations, higher tissue levels of manganese are usually found in the older leaves on the plant and may be associated with damaged or diseased leaves. Mn varied in the range of 0.10-4.77 mg/g. It is considered an essential metal to controlling the behavior of several micronutrients in the soil, but it may cause severe problems if found in high levels. Various reports indicating the high application of Mn in agriculture are available [35]. Although Zn is an essential trace element, high levels can cause harmful health effects. Zn varied in the range of 43.29-1293 μg/g, where 70% of samples were estimated to be more than the maximum permissible level cited by CCME, indicating that there is relatively Zn pollution and relating to the application of Zn fertilizer. Barium (Ba) concentrations range was 21.21 μg/L in the irrigation water samples. The Ba concentrations higher than the CCME limit (100 μg/L) for irrigation water. The US Environmental Protection Agency found that acute exposure to Ba at above the maximum contaminant level (2 mg/L) can potentially cause gastrointestinal disturbances and muscular weakness. Long-term exposure to Ba at can also potentially cause hypertension. There is no evidence that lifetime exposure to Ba in drinking water has the potential to cause cancer [33]. Other elements from Cr to As (Cr > Ni > Cu > Pb > Cd > As) were exist in the trace concentrations. The mean values of Cr, Ni, Cu, Pb, Cd, and As did not exceed the Canadian soil guidelines, which mean that the soil is not contaminated. Zn were present in high levels and had a significant contamination level compared to other elements.
Table 3 Summary of elements concentration (µg /g) in Hail soil

| Analytical techniques | Data obtained from Flame photometer | Data obtained from ICP-MS |
|-----------------------|-------------------------------------|--------------------------|
| Variable              | Na   | K     | As    | Cd    | Pb    | Cr    | Ni    | Fe    | Mn    | Ba    | Cu    | Zn    |
| Max                   | 1869 | 825   | 0.001 | 0.2611| 5.152 | 15.715| 14.2205| 5145  | 137.865 | 21.21 | 7.588 | 75.495 |
| Min                   | 24   | 54    | 0.001 | 0.001 | 0.31591| 1.93445| 1.12665| 738.85| 10.752 | 2.6124 | 0.57645| 1.0913 |
| Median                | 135  | 297   | 0.001 | 0.00791| 1.26525| 6.1495| 5.4775 | 2906.4| 44.77  | 13.2685| 1.27667| 28.882 |
| Mean                  | 241.133| 360  | 0.001 | 0.02721| 1.57276| 6.5997| 5.76274| 2825.75| 12.1469| 7.21277| 12.3198| 29.1399 |
| SD                    | 532.734| 237.583| 0.0241 | 0.76183| 3.28753| 3.0612| 711.13 | 29.5262| 4.89786| 1.43869| 16.6138 |
| CCME                  | 45   | -     | 100   | 104   | 70    | 64    | 45    | 5000  | 200   | 100   | 63    | 200   |

3.3 Comparing the trace elements in the study area to the soil in other regions in Saudi Arabia

The present results recorded high levels of Zn, Cu, Ni, and Cr than the other regions (Table 4). The abundance of individual elements in soils and other surficial materials e.g. Na is determined not only by the element content of the bedrock or other deposits from which the materials originated, but also by the effects of climatic and biological factors as well as by influences of agricultural and industrial operations that have acted on the materials for various periods of time. In the agricultural Hail soil, Na values range was 0.19-4.81 mg/g. While, the Al concentrations varied in the range of 10.26-81.26 mg/g (Table 5). The soil pH is the most critical factor controlling the amount of Al\(^{3+}\) available for plant uptake in the soil solution.
Table 4 levels of elements in the soil of some cities in Saudi Arabia (µg /g)

| City                                      | Zn       | Cu     | Ni      | Cr      | Pb      | Cd      | Co      | Se      | Al  |
|-------------------------------------------|----------|--------|---------|---------|---------|---------|---------|---------|------|
| Al-Qassim region (AL-WABEL et al. 2017)   | 1645.40  | ND-15.9| ND-14.4 | 8.10-28.10 | 6.5-149 | ND-5.40 | ND-3.80 | -       | -    |
| Al-Hassa Oasis (MOHAMMED et al., 2014)    | 15.45-40.16 | 26.61-57.33 | 4.32-10.14 | 2.77-4.14 | 0.04-0.08 | 2.46-4.14 |
| Northwestern, Saudi Arabia (NAZZAL et al. 2016) | 10.9-52.2 | 5.8-42.8 | 14.8-37.6 | 15.9-62.4 | 0.09-0.78 | 0.9-4.9 |
| Al-Kharj region, (AL-HAMMAD & ABDEL-SALAM, 2016) | 38.45-174.52 | - | 14.70-49.52 | 43.50-89.23 | 18.71-42.85 | 0.194-0.475 | 21.87-91.34 | - | - |
| Gulf of Aqaba (GHREFAT et al. 2016)       | -        | -      | -       | -       | -       | -       | -       | 0.1-3    | 0.5-6.8 |
| Al-Hayr area- Riyadh (HASAYAN et al. 2017) | 9.52-27.40 | 8.86-10.91 | 11.13-19.23 | 10.48-20.30 | 5.60-7.14 | 0.06-0.16 | - | - | - |
| Present study                             | 43.29-1293.31 | 8.44-105.51 | 3.67-86.93 | 6.28-140.05 | 1.66-90.31 | 0.12-2.09 | 0.86-48.27 | 0.40-8.90 | 0.72-245.6 |

Table 5 Summary of major elements concentration (µg/ g) in Hail soil

| Variable | Na        | Mg        | Ca        | Al         |
|----------|-----------|-----------|-----------|------------|
| Max      | 117.19    | 74.16     | 39.35     | 245.57     |
| Min      | 1.90      | 2.34      | 0.19      | 0.72       |
| Median   | 9.54      | 7.03      | 0.69      | 18.16      |
| Mean     | 15.12     | 9.40      | 2.54      | 27.28      |
| SD       | 18.70     | 10.77     | 5.97      | 35.90      |
Calcium and Magnesium are secondary nutrient and plants require them in quantities as phosphorus. Where, Ca and Mg ions held to the surface of clay and organic matter in the soil by electrostatic charge. When Ca and Mg are abundant in the soluble phase tree roots absorb these nutrients by mass flow. If Ca and/or Mg are less abundant or limited by soil moisture, uptake occurs more slowly through diffusion. The Ca and Mg in soil varied considerably in Hail area, where the ranges were 1.90–37.99 and 2.34–74.16 mg/g, respectively (Table 5). For Na, Al, Ca and Mg, no significant differences were observed between all soil samples.

3.4 Contamination level of elements

3.4.1 I-geo values

The result of I-geo values in the soil samples were presented in Table 6 and were mostly fell on the negative site, where, the ranges were not very wide. I-geo values for Zn showed that 43% of the samples fell in the unpolluted class, 28% in the unpolluted–moderately polluted category, 26% are somewhat polluted and 4% are moderately to strongly polluted. I-geo values for Cu, Ni and Cr showed that more than 89% of the samples fell in the uncontaminated class. While I-geo for Pb, Cd, and Co showed that 100% of the samples fell in the unpolluted category. Finally, I-geo for Se showed that 2% of the samples dropped in the uncontaminated class and 24% in the unpolluted–moderately polluted level, 46% are moderately polluted, and 28% are moderately to strongly polluted. I-geo values in the analyzed soils revealed no real sign of contamination with almost all the samples reflecting a lack of contamination for all elements except Se and Zn, which showed a moderate level of pollution due to anthropogenic sources. These are suggested the absence of the variety of soil features and pollution sources in the studied area [2].

Table 6 I-geo value of trace elements in Hail soil

| Variable | Max    | Min    | Mean   | Median  | SD      | Soil quality         |
|----------|--------|--------|--------|---------|---------|----------------------|
| Na       | 15.77494 | 9.491853 | 11.71383 | 11.98371 | 1.724339 | Extremely polluted   |
| AS       | -3.906890596 | -3.906890596 | -3.906890596 | 0 | Unpolluted |
| Cd       | -2.03686 | -10.0653 | -7.24821 | -7.08164 | 2.494175 | Unpolluted           |
| Pb       | 7.909453 | 3.881906 | 5.910909 | 5.883743 | .945549 | Extremely polluted   |
| Cr       | 7.78017 | 3.752623 | 5.781626 | 5.75446 | 0.945549 | Extremely polluted   |
| Ni       | 8.736791 | 5.07893 | 7.140423 | 7.360408 | 0.995346 | Extremely polluted   |
| Fe       | 24.03171 | 21.23189 | 23.02289 | 23.20777 | 0.716055 | Extremely polluted   |
| Mn       | 14.16601 | 10.48543 | 13.00226 | 13.46438 | 0.988808 | Extremely polluted   |
| Ba       | 10.46557 | 7.44427 | 9.467148 | 9.788827 | 0.824032 | Extremely polluted   |
| Cu       | 8.316037 | 4.597585 | 6.807031 | 6.86051 | 0.938145 | Extremely polluted   |
| Zn       | 13.2972 | 7.184941 | 11.22702 | 11.91099 | 1.802304 | Extremely polluted   |
3.5 Nemerow pollution index

The values, range, mean and SD for $P_i$, Nemerow P and PLI in the samples were shown in Table 7. The single index ($P_i$) clarified that the Zn and Se pollution intensity was strong, where the pesticides and fertilizers were the well-known external sources of agricultural soil elements in addition to natural causes [36, 37]. PLI did not show much fluctuation, where 4.2% of samples showed high levels (>1). Lower values of PLI imply no considerable input from anthropogenic sources. Nemerow P for Zn, Cu, Ni, Cr, Se and Cd was more than 1 indicating slight overall pollution, while for Co and Pb, it was less than 1, showing no contamination. The levels of elements in agricultural soils are mainly affected by parent materials in addition to pesticide and fertilizer application [36, 37].

Table 7 Descriptive statistics of soil trace elements pollution indices

| Variable | Max  | Min  | Mean  | SD    | $P$  |
|----------|------|------|-------|-------|------|
| $P_i$    |      |      |       |       |      |
| Na       | 41.5333 | 0.53333 | 5.35873 | 9.11276 | 1332.536 |
| K        | -    | -    | -     | -     | 636.4845 |
| As       | 0.0001 | 0.0001 | 0.0001 | 0     | 0.001 |
| Cd       | 0.00251 | 0.00026 | 0.00055 | 0.185625 |
| Pb       | 0.0736 | 0.00451 | 0.02247 | 0.01544 | 3.808918 |
| Cr       | 0.24555 | 0.03023 | 0.10312 | 0.05528 | 12.05233 |
| Ni       | 0.31601 | 0.02504 | 0.12806 | 0.07823 | 10.84969 |
| Fe       | 1.029 | 0.14777 | 0.56515 | 0.22927 | 4150.654 |
| Mn       | 0.68933 | 0.05376 | 0.36573 | 0.17759 | 110.3567 |
| Ba       | 0.2121 | 0.02612 | 0.12128 | 0.05658 | 17.27637 |
| Cu       | 0.12044 | 0.00915 | 0.05054 | 0.02886 | 5.818741 |
| Zn       | 0.37748 | 0.00546 | 0.1457 | 0.10696 | 57.22162 |
| PLI      | 0.08593 | 0.01364 | 0.0452 | 0.02077 |

3.6 Descriptive statistics of the EF values of soil trace elements

Table 8 EF value of trace elements in Hail soil mg/kg

| Max     | Min    | Mean    | SD     | Pollution level |
|---------|--------|---------|--------|-----------------|
| Na      | 46.6824 | 1.02138 | 8.84561 | significant     |
| As      | 6.77*10^{-5} | 9.72*10^{-6} | 2.24*10^{-5} | Clean light     |
| Cd      | 0.0056 | 1.54219 | 0.000496 | 0.001198 | Clean-light     |
| pb      | 0.12157 | 0.0121 | 0.04292 | 0.02571 | Clean-light     |
| Cr      | 0.58686 | 0.05145 | 0.19782 | 0.1107 | Clean-light     |
| Ni      | 0.40552 | 0.06922 | 0.21958 | 0.07909 | Clean-light     |
| Fe      | 1      | 1       | 1      | 0    | Clean-light     |
Mn | 1.97499 | 0.32175 | 0.65946 | 0.35329 | Clean-light
---|---|---|---|---|
Ba | 0.5077 | 0.097 | 0.22116 | 0.0913 | Clean-light
Cu | 0.1569 | 0.05064 | 0.08657 | 0.02748 | Clean-light
Zn | 0.68544 | 0.01741 | 0.24658 | 0.17271 | Clean-light

Table 8 summarized the descriptive statistics of the EF values of soil trace elements. Where, the highest EF values (mean > 20) of soil trace elements recorded for Zn and Cd, which indicated substantial pollution influenced by anthropogenic sources [36,37]. The average EF value of Cu, Ni and Pb were more than 5, suggesting that they had been impacted by natural or anthropogenic sources. The average EF values of Mn, Cr, and Co were comparable; their EF values were less than 5, where, the soil sampling sites had moderate pollution. Finally, for Fe the EF values were less than two suggested that the elements come entirely from crustal materials or natural processes.

### 3.7 Total Dissolved Solids (TDS)

The total concentrations of soluble salts in water have great effects on plants and different crops. If the salt concentration in water increases, it is difficult for plant to extract water. The irrigation water quality classification schemes have been proposed by many researchers. Those classifications depend on one or more factors; one of the most important factors is salinity of water which expresses by TDS. Wilcox and Magistad (1943) adopted more simplified classification as given in table (8). Also, another classification is there as shown in table (9), according to (FAO, 1985). [38,39].

| Water class | EC (Mhos/cm²) | Salt content (mg/l) | Sodium (%) | Boron (ppm) |
|-------------|--------------|---------------------|------------|-------------|
| Class 1     | 1000         | 700                 | 60         | 0.5         |
| Class 2     | 1000-3000    | 700-2000            | 60-75      | 0.5-2.0     |
| Class 3     | >3000        | >2000               | >75        | >2.0        |

Class 1: Excellent to good, suitable for most plants most conditions; Class 2: Good to injurious, probably harmful to more sensitive crops; Class 3: Injurious to unsatisfactory, probably harmful to most crops.

### 4. Conclusion

From the present experimental study, we can have concluded the following point:

- Agriculture soil contamination were studied using analytical calculation and comparison using ICP-MS and flame photometer technique.
- The mean of the elements concentrations in irrigating water were found as the following order: Na > K > Mn >Ba > Fe > Zn > Pb > Cr > Ni > Cu > Cd > As.
- The mean of the elements concentrations in soil were found as the following order: Na > K > Fe > Mn > Zn > Ba > Cr > Ni > Cu > Pb > Cd > As.
- the mean values of Cr, Ni, Cu, Pb, Cd, and As, did not exceed the Canadian soil guidelines, which mean that the soil is not contaminated. Zn were present in high levels and had a significant contamination level compared to other elements.
- Nemerow P, I-geo, and PLI indices were successfully applied for the assessment of elemental contamination of Hail soil. However, the highest EF values (mean > 20) of soil trace elements was recorded for Zn and Cd, which indicated heavy pollution influenced by anthropogenic sources.
- The EF values for Se were less than two suggested that the element comes mainly from a geological source; however, the anthropogenic activities related to use of fertilizers in the agricultural lands may have led to an increased amount of this element in the soil.
Consequently, the risk of Cd and Zn accumulation in Hail soil requires further attention and monitoring to make sure the agrochemical inputs are responsible for the high accumulation of elements in soil.

The used irrigation water as soon as agriculture soil at Hail region Saudi Arabia are suitable and considered as a good soil comparison with the international standards.

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