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Assessment of Trace Elements Contamination of Irrigation Water and Agricultural Soil in Hail Region, Saudi Arabia

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Abstract: *The determination of trace elements in water is of widespread importance. The concentrations of elements in the ground water used for irrigation in Hail region (Saudi Arabia) were determined. The trend of elements according to mean concentration was: B > Fe> Ba> Al > Cr > Cu > Mo > Se >Mn>Ni >V > Co >Pb>Sb> As > Cd> Ti.All elements level wasin the permissible levels according to CCME (2007) exceptfor Cr and Ba levels wereabove the limit. The study also, focused on the behavior of Fe, Mn, Zn, Cr, Pb, Ni, Cu, Co, Se and Cd in agricultural soil (50 samples)in Hail region. The study showed considerable variation in the levels of the analyzed elements in the soil samples. The total metal concentrations in samples ordered as follows: Fe >Mn> Zn > Cr >Pb> Ni > Cu > Co > Se > Cd. According to soil quality guidelines, there was a slight risk from Cu, Ni and Cr and a considerable risk from Zn and Se. The geoaccumulation (I-geo), single pollution, Nemerow pollution indices showed that the Se pollution intensity was significant for agricultural soils. This variation in concentration conducted to the intensity of agricultural activities. I-geo values revealed no real sign of contamination with almost all the samples, reflecting a lack of contamination for all elements except Se and Zn. While the enrichment factor (EF) for Fe and Se were less than 2 suggested that the elements come entirely from crustal materials or natural processes. Also, the EF values for Zn and Cd (mean > 20), indicated heavy pollution influenced by anthropogenic sources.*

Keywords: *Saudi Arabia, Hail region, groundwater, agricultural soil, trace elements*

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I. Introduction

Groundwater is one of the most important natural resources for domestic, agriculture and industrial uses in an arid country like Saudi Arabia. Rapidly depleting groundwater aquifers in Saudi Arabia as a result of high population growth and rapid industrialization are threatening this vital natural resource both in terms of quantity and quality. To evaluate the suitability of groundwater resources for different uses, an understanding of their chemical composition is essential [1].

Certain trace elements are needed by humans in minute quantities for adequate growth and development and to maintain proper physical functions. Some trace elements are essential to health, and these micro minerals are present in enzymes, hormones, and cells. Inadequate and excessive intakes of some of these trace elements may cause contrasting effects on health[2]

Trace elements can be categorized as (1) essential to human life (chromium, copper, iodine, molybdenum, selenium, and zinc), (2) probably essential (boron, manganese, nickel, silicon, and vanadium), and (3) potentially toxic, some of which possibly have essential functions (aluminum, arsenic, cadmium, fluoride, lead, lithium, mercury, and tin) [3].

Epidemiological studies in recent years have indicated a strong association between the occurrences of several diseases in humans,particularly cardiovascular diseases, kidney related disorders, neurocognitive effects and various forms of cancer, and the presence of trace metals such as Cd, Al, Cr and Ni. Excessive or deficient levels of essential micronutrients such as cobalt, chromium, copper and zinc may also have detrimental effects on health [4]. Metal contaminants can easily enter to food chain if contaminated water, soils and/ or plants are used for food production.

The main source of irrigation water in Hail's the groundwater [5]. In the arid environment, the salinization of agricultural soil is a severe problem due to the high evaporation condition and usage of marginal quality water for irrigation along with low rainfall. These depend on many factors such as soil geology and properties, climate, land drainage and finally crop and water manage [6].

The soil is a crucial part of the Earth system as it controls the hydrological, erosional, biological, and geochemical cycles. The soil system also offers goods, services, and resources to humankind. This is why it is necessary to research how soils are affected by societies. Pollution is one of these damaging human activities, and we need more information and assessment of soil pollution [7]. Soils are used to detect the deposition, accumulation, and distribution of trace elements in different locations [8]. Since the soil is a thin part of the earth surface system that comes into direct contact with a man [9], therefore, it can transfer pollutants to the food chain. Thus, it is vital to preserve the soil conditions for sustainable development [10].

Contamination of soils by trace elements, such as Cd, Ni, Zn, Pb, and Cu, was increased dramatically during the last few decades [11]. The mining, smelting, manufacturing, use of agricultural fertilizers and pesticides, municipal waste, traffic emissions, and industrial effluents are the main factors affecting their distribution [11, 12]. Land degradation caused by trace elements has a significant adverse effect on the environment and ecosystem worldwide. Dispersion of trace elements in irrigated soils and the growing plants, resulting in the contamination of food that may have hazardous to humans and animals. [1] stated that the total metal concentrations in Hail soil samples ordered as follows: Cd<Pb≈Ni≈Cu<Cr<Zn<Mn<Fe, where there is a slight risk from Ni and Zn and a considerable risk from Cd.

Vegetables and fruits cultivated in soils polluted with toxic and trace elements take up such elements and accumulate them in their non-edible and edible parts with high amounts, and there is no mechanism for their elimination from the human body [13]. The present study aims to investigate the distribution of some elements in the irrigation water and agricultural soil at Hail region to assess the elements contamination levels.

II. Materials and methods

2.1. Study area

This study was conducted during 2016 in Hail region, and its Villages[14]. 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[15].

2.2. Water collection and analysis

Ground water samplesused for irrigation were collected and preserved according to the operating procedure for groundwater sampling [16]. A total of fifty samples were brought from several farms within the Hail area. Well Tight-capped high quality polyethylene 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 [17]. 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 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 2016. The samples were collected from the upper 10 cm sections. After grinding and sieving through 2 mm mesh, 500 mg were digested according to [18]. 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[19];

$$PLI = (P_{i1} x P_{i2} x P_{i3} x \dots \dots . P_{in})^{\frac{1}{n}}$$

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 (Si):

$$P_i = C_i / S_i$$

Where PLI value >1 would indicate a contaminated site while PLI value <1 indicates no contamination.

2.4.2. Geoaccumulation index

I-geo was computed as follows, [20].

$$I - geo = \log_2\left(\frac{C_n}{1.5B_n}\right)$$

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) ofZn (200), Cu (63), Pb (70), Ni (45), Co (40), Cr (64), Se (1) and Cd (1.4) in the Canadiansoil 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}	I_{geo}<0	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[22]. The following equation determines P:

$$P = \sqrt{\frac{{P_{max}}^2 + {P_{ave}}^2}{2}}$$

2.4.4. Enrichment factor

The EF of a single trace element in the soils was calculated as follows [23]:

$$EF = \frac{\left(\frac{M}{Al}\right)_{sample}}{\left(\frac{M}{Al}\right)_{background}}$$

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 TAYLORand MCLENNAN[25] were used. EF valueswere 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 elementsfractions among different locations by ANOVA test.

III. Results and Discussion

Table 2 shows 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: B > Fe> Ba> Al > Cr > Cu > Mo > Se >Mn>Ni >V > Co >Pb>Sb> As > Cd> Ti. The variation in trace elements concentration is controlled by the variation in local and regional geology, water/rock interactions, dilution due to precipitation [5].

Boron (B) concentration values were ranged from 1136.48 to 12234.62 µg/L in the irrigation water samples. Humans are primarily exposed to B through the consumption of food and drinking water [26]. Dermal exposure to B has not been found to be a danger to humans, although B can enter the body through contact with damaged skin [27]. Toxicity associated with exposure to B is currently controversial. Aluminum (Al) concentrations were ranged between42.78 and 588.26 µg/L in water samples. These concentrations are well below the Canadian Environmental Quality Guidelines [21]for irrigation water. The main source of human exposure of Al is diet. Al has been considered to be a causative agent for various neurological disorders, including Alzheimer's disease [28].

Vanadium (V) was a transition metal; it can be found both in groundwater and in surface water and its concentration depends on environmental parameters. The V concentrations range was 0.73 – 24.87 µg/L in the irrigation water samples. This concentration is within the limits allowed by classification of [21]). Chromium (Cr) concentrations range was 1.44 –278.23 µg/L in the samples. The Cr mean concentration was 86.74 µg/L. It is much higher than the CCMEguidelines. Primarily, exposure to Cr may occur from natural or industrial sources. The major target organ for chromium toxicity is the respiratory tract. Acute exposures cause shortness of breath, coughing, and wheezing while perforations and ulcerations of the septum, bronchitis, decreased pulmonary function, pneumonia, and other respiratory effects were reported from chronic exposure [29]. The International Agency for Research on Cancer (IARC) has determined that chromium compounds are carcinogenic to humans [30]. Manganese concentrations range was 4.02 –82.14 μg/L. Mn concentrations were much lower than the CCME guidelines [21]. Manganese is an essential nutrient, and eating a small amount of it each day is important to stay healthy[30]. Iron (Fe) concentration ranged from 75.24 to 4979.5 μg/L. High levels of iron can cause irritability in the gastrointestinal tract and can affect water's taste by enhancing the growth of iron bacteria. Also, it has the potential of staining metal and laundry pipes for reticulation [31].

Cobalt (Co) is a very toxic heavy metal ion and its containing compounds are widely used in many industrial applications such as mining, electroplating, metallurgy, paints, pigments and electronic Stern [32]. The presence of cobalt in the environment leads to several health troubles such as low blood pressure, vomiting, nausea, heart diseases, vision problems, sterility, thyroid damage, hair loss, bleeding, diarrhea, bone defects and may also cause mutations (genetic changes) in living cells [33]. The Co concentrations range was 0.05–11.02μg/L in the irrigation water samples, while nickel (Ni) concentrations were varied from 0.05 to 28.78 μg/L in the samples. None of the Ni concentrations exceeded the permitted limits of CCME for irrigation water. However, Ni present in some groundwater because it can be dissolved from rocks that bear Ni ore. The International Agency for Research on Cancer[34]concluded that Ni is carcinogenic to humans when it is ingested at higher than normal concentrations. Ni is the most common cause of al lergic contact dermatitis, particularly in women.[35]stated that consuming groundwater polluted with Ni can lead to a high risk of developing lung, nose, and larynx cancer and respiratory failure.

Copper (Cu) concentrations range was 0.42 –169.91 μg/L in the irrigation water samples. These concentrations were well below the CCMElimits. Cu is an essential nutrient, but some people exposure long-term at such concentrations may cause liver or kidney damage. It has been shown that high doses of Cu cause stomach and intestinal distress, liver and kidney damage, and anemia. The symptoms of acute Cu toxicity are headache, nausea, vomiting, gastrointestinal irritation, hemorrhage, hemolysis, and multi-organ dysfunction syndrome [36].Arsenic (As) concentrations ranged from 0.10 to 1.69 μg/L in the irrigation water samples. As naturally enters groundwater through the dissolution of minerals as the groundwater percolates through rocks containing as, but it can also be released because of agricultural and industrial practices. Currently, many parts of the world have been affected by chronic As poisoning, and it has become a global environmental and public health. The most common and earliest nonmalignant effects related to chronic As exposure are skin lesions [37].

Selenium (Se) concentrations was varied in the range of 5.00 –180.64 μg/L in the irrigation water samples. None of the samples contained Se concentrations higher than the limits that have been set for irrigation water by CCME. Usually in areas where high levels of Se in the soil contribute to the Se content of the water. Exposure to high levels of Se in food and water causes discoloration of the skin, pathological deformation and loss of the nails, loss of the hair, excessive tooth decay and discoloration, garlic odor in breath and urine, lack of mental alertness, and listlessness [38]. Molybdenum (Mo) concentrations range was 0.28–139.34 μg/L in the irrigation water samples. Mo is an essential element in animal and plant nutrition [39]. Both deficiencies and excesses can cause health problems, so there is considerable interest in the level of Mo and its activity in the environment. Conversely, excessive Mo reduces the uptake of copper in the human body and leads to skeletal deformities [40].

Cadmium (Cd) concentrations range was 0.05–1.96 μg/L in the irrigation water samples, the concentrations were much lower than the CCMElimits (5.1 μg/L)for irrigation water. Occurrence of Cd in the environment is from both natural and anthropogenic sources. Cd is considered to be highly toxic elements and producing symptoms such as nausea, vomiting, respiratory difficulties, cramps, and loss of consciousness at higher doses. Anemia, anosmia (loss of sense of smell), cardiovascular diseases, renal problems, and hypertensionmanifested in human due to chronic exposure to Cd [41].Antimony (Sb) concentration varied between 0.06 and 1.33 μg/L in the irrigation water samples. This element naturally occurs at low concentrations in the environment. Sbis essential micronutrients for plants, animals and humans, but at high concentrations may cause toxicity and harm human health because of this non‑biodegradable nature, which causes them to readily accumulate in tissues and living organisms[42].

Barium (Ba) concentrations range was 4.22–685.58 μg/L in the irrigation water samples. The Ba concentrations higher than the CCMElimit (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 [43].

Thallium (Tl) was detected in very small concentrations, in irrigation water samples 0.00-0.29 μg/L. If large amounts Tl are eaten or drunk for short periods of time, then it can affect the nervous system, lung, heart, liver, and kidney. Temporary hair loss, vomiting, and diarrhea can also occur, and death may result after exposure to large amounts of Tl for short periods. Lead (Pb) concentrations varied from 0.10to 3.34 μg/L in the irrigation water samples. Pb can enter into groundwater and surface water from the atmosphere or soil. Excessive amount of Pb can damage various systems of the body, including the nervous system, reproductive systems, and the kidneys, and it can cause high blood pressure and anemia. Learning disabilities, behavioral changes, and impairment of intellectual functions are consequences high blood Pb levels in children. At very high levels of Pb, exposure resulted in convulsions, coma and death [44]. The U.S. Environmental Protection Agency (US EPA) and the International Agency for Research on Cancer (IARC) have determined that inorganic Pb is likely carcinogenic in humans.

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

Variable	Max	Min	Median	Mean	SD	CCME (2007)
B	12234.62	1136.48	1910.00	3304.88	3431.67	-
Al	588.26	42.78	225.68	233.54	145.10	5000
V	24.87	0.73	7.38	9.16	6.46	100
Cr	278.23	1.44	68.83	86.74	76.75	8
Mn	82.14	4.02	15.72	24.13	24.84	200
Fe	4979.50	75.24	479.67	769.67	1295.79	5000
Co	11.02	0.05	0.30	1.04	3.05	50
Ni	28.78	0.05	6.68	9.93	9.85	200
Cu	169.91	0.42	13.39	41.45	60.16	-
As	1.69	0.10	0.21	0.46	0.51	100
Se	180.64	5.00	11.53	29.09	49.50	-
Mo	139.34	0.28	25.27	33.95	39.78	-
Cd	1.96	0.05	0.13	0.29	0.52	5.1
Sb	1.33	0.06	0.38	0.55	0.44	-
Ba	685.58	4.22	316.89	340.50	253.20	100
Tl	0.29	0.00	0.10	0.09	0.08	-
Pb	3.34	0.10	0.25	0.57	0.93	200

The perusal soil data revealed that, the trend of elements according to mean concentration was: Fe >Mn> Zn > Cr >Pb> Ni > Cu > Co > Se > Cd. 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 [45].

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 [46], so theFe 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 [47].

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 [48].

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. Cu also covers the class of essential heavy metals but may prove highly toxic if present in more than guidelines limits. Cu ranged from 8.4 to 105.5 µg/g, where 15 % of the samples contained Cu more than the permissible level.

Cr is a non-essential metal and toxic for all living beings; it has two forms found in the environment, hexavalent and trivalent depending on redox conditions and pH. In aerobic conditions, Cr (VI) was the dominant form of Cr in shallow aquifers. Cr (VI) can be reduced to Cr (III) by soil organic matter, S^{2-} and Fe^{2+} ions under anaerobic conditions. The toxic Cr level in the soil is around 60 µg/g [47]. Cr measurements, with a mean value of 52.20 µg/g revealed an increase of Cr in 36% of samples making it reach about 140 µg/g. Nicomes mainly from natural sources, where the critical level for Ni in soil is 45 µg/g [21]. Ni varied in the range of 3.67-86.39 µg/g, where the percentage of Nicontamination in the studied areas was about 28%. The anthropogenic inputs like manure and fertilizers have lower levels of Ni and Cr than those already found in the soil [49].

Pb is the least mobile among the heavy metals. It is not essential, but toxic to plants. Pb in soil samples collected from the Hail soil and their village ranged from 1.66-90.31 µg/g with mean value 35.07 µg/g. The soil Pb concentration in 4% of the samples was more than the permissible level 70 µg/g reflecting the aerial deposition from the vehicle exhaust.

Cd enters the environment through the uncontrolled burning of garbage and coal and enters the food chain indirectly or directly from plants or animals [50]. Cd is also present as an impurity in several products, including detergents, phosphate fertilizers and refined petroleum products. The Cd concentration in the soils was relatively low; it varied in the range of 0.12-2.09µg/g, where about 6% of the samples exceeded the guideline ofCCME. Overall, there is no significant Cd contamination in the studied areas.

Se is a potentially toxic element, and mining-related Se release was a significant concern during the last decade. It varied in the range of 0.40-8.90 µg/g. The percentage of Se contamination according to the guideline ofCCMEwas about 75%. Overall, the increase in Se concentration may be due to the addition of Se to fertilizers. Also, rainfall plays an essential role in determining Se content in soil [51]. In high rainfall areas, if the parent rock is rich in Se, the soil contains a high amount of Se, but it is bound to iron in a poorly soluble complex. It is found that Se binds to clay fractions more readily because of its high specific area and Se content is found to decrease with increasing depth. Se adsorbs less to coarse and fine sand fractions. Se binds well with organic matter in acid soils [52].

Table3: Summary of elements concentration (µg /g) in Hail soil

Variable	Se	Co	Cd	Pb	Cr	Ni	Cu	Zn	Mn	Fe
									(mg /g)	(mg /g)
Max	8.90	48.27	2.09	90.31	140.05	86.39	105.51	1293.31	4.8	230.7
Min	0.40	0.86	0.12	1.66	6.28	3.67	8.44	43.29	0.101	7.170
Median	4.55	7.90	0.47	30.01	38.70	29.84	23.47	367.14	0.492	17
Mean	4.88	10.68	0.60	35.07	52.20	34.29	33.25	470.66	0.623	22.5
SD	2.13	9.31	0.43	18.30	32.28	18.70	25.54	381.22	0.685	33.01
CCME	1	40	1.4	70	64	45	63	200		

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**

Ca and Mg 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 2.34-74.16mg/g, respectively (Table 5). For Na, Al, Ca and Mg, no significant differences were observed between all soil samples.

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

Contamination level of elements

The result of *I-geo*values in the soil samples were presented in Table 6and 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 moderated 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 moderated 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 [5].

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

Variable	Min	Max	Mean	Median	SD	Soil quality
Zn	-2.79	2.11	0.02	0.29	1.52	Moderately to heavily polluted
Cu	-3.48	0.16	-1.90	-2.01	1.07	Unpolluted to moderately polluted
Ni	-4.20	0.36	-1.20	-1.18	0.84	Unpolluted to moderately polluted
Cr	-3.93	0.54	-1.15	-1.31	0.92	Unpolluted to moderately polluted
Pb	-5.98	-0.22	-1.78	-1.81	0.87	Unpolluted
Cd	-4.07	-0.01	-2.11	-2.14	0.92	Unpolluted
Co	-6.12	-0.31	-2.89	-2.92	1.07	Unpolluted
Se	-1.92	2.57	1.54	1.60	0.79	Moderately to heavily polluted

The values, range, mean and SD for P_i, Nemerow P and PLI in the samples were shown inTable 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 [53].

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.

NemerowP 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 [53].

Table 7. Descriptive statistics of soil trace elements pollution indices

	Variable	Min	Max	average	SD	*P*
pi	Zn	0.22	6.47	2.35	1.91	4.87
	Cu	0.13	1.67	0.53	0.41	1.24
	Ni	0.08	1.92	0.76	0.42	1.46
	Cr	0.10	2.19	0.82	0.50	1.65
	Pb	0.02	1.29	0.50	0.26	0.98
	Cd	0.09	1.49	0.43	0.31	1.10
	Co	0.02	1.21	0.27	0.23	0.87
	Se	0.40	8.90	4.88	2.13	7.18
PLI		0.14	2.07	0.73	0.35	

Table 8summarized 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 (SZOLNOKI et al. 2013) [54]. 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 and Se, the EF values were less than two suggested that the elements come entirely from crustal materials or natural processes.

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

	Mn	Fe	Zn	Cu	Ni	Cr	Pb	Cd	Co	Se
Mean	**2.29**	**1.27**	**30.00**	**6.36**	**1.79**	**1.65**	**17.98**	**24.68**	**1.40**	**235.19**
SD	**1.87**	**1.11**	**28.88**	**22.48**	**2.22**	**1.89**	**23.36**	**44.01**	**1.19**	**572.77**
Min	**0.66**	**0.02**	**1.29**	**0.47**	**0.25**	**0.26**	**3.01**	**3.19**	**0.49**	**41.30**
Max	**11.58**	**8.17**	**121.05**	**140.00**	**16.05**	**13.68**	**165.39**	**291.77**	**7.35**	**4017.51**
Pollution level	**moderate**	**light**	**strong**	**significant**	**light**	**light**	**significant**	**strong**	**light**	**extreme**

IV. Conclusion

For agricultural soil, the mean values of Cu, Ni, Cr, Pb, Cd, and Co did not exceed the Canadian soil guidelines, which mean that the soil is not contaminated. Se and Zn were present in high levels and had a significant contamination level compared to other elements. NemerowP, *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.

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