

CHEMICAL ANALYSIS AND ENVIRONMENTAL IMPACT OF HEAVY METALS IN SOIL OF WADI JAZAN AREA, SOUTHWEST OF SAUDI ARABIA

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Abstract. A few investigations have been done on characterizing heavy metals at Jazan district, mostly done as analyses of heavy metals associated with water, sediments and shrimps. The current study was carried out mainly to evaluate and characterize heavy metals concentrations in soils of the main Wadi Jazan and its tributaries in order to determine its environmental impacts. The heavy metals were measured by using ICP-MS. Results indicate that soil of Wadi Jazan area has different concentrations of heavy metals; some of them have economic importance such as Au, Ag and U, some other considered useful for the environment (Such as Cu, Se and Zn) and others are harmful for the environment (Such as Cd, Pb, and others). The most extremely soil pollution at Wadi Jazan is by Cd, where all analyzed samples have higher concentration than the maximum permissible concentration by the World Health Organization. Heavy metals concentrations along Wadi Jazan indicate that the most polluted area is located around Abu Arish City. The current investigation conclude that there are a direct effect of the harmful heavy metals on plants, terrestrial animals, fishes and marine organisms and human; due to the ability of these heavy metals to reach and entered the food chain, and hence causes different types of harmful effects and diseases. Present study refers also to the suitability of some recent techniques for soil remediation at Wadi Jazan, such as engineering remediation (Replacement of contaminated soil, soil removal, soil isolation and adsorption) and bioremediation (Phytoremediation).

Keywords: *environment, metals pollution, health risk assessment, sediments, Saudi Arabia*

Introduction

Minerals and rocks are important role in our lives due to their many benefits for humans, especially as they intervene in every industrial, agricultural and economic needs (Mart, 2014). The extent of nations and peoples progress is measured by its ability to find out what their lands contain from metals and rocks of economic value and also minerals and rocks which have a harmful impact on the environment and its components (Uluturhan et al., 2011). Soil pollution by heavy metals is considered one of the hot topics all over the world due to its direct and indirect impact on human health. The main objective of the current work is to analyze and characterize heavy metals in soil of Wadi Jazan, in addition the determination of its environmental impacts.

The most harmful minerals to the environment are arsenic, asbestos, cadmium, lead, mercury, manganese, antimony, zinc, barium, beryllium, bismuth, bromine,

chlorine, thallium and uranium. Recently it is approved that the aluminum is considered as a highly toxic metal (El Tahlawy, 2007). Most of these minerals present in the rocks and nature in very small amounts and for a long time, but as a result of erosion, decomposition and transportation of the exposed rocks by rains, flood, winds and others, as well as the extraction of these metals and their use in the industry led to many environmental and health problems that were not known before (Nadia et al., 2009). Usually these health problems arise due to these heavy metals replace other metals found in the body and perform important role in the organic function. For example, cadmium replaces zinc and lead eliminates calcium anywhere, and when concentrated cadmium or lead in the bone or tissue happens, it becomes difficult to get rid of them and they cannot be able to carry out the operations which were carried out by the original elements. This of course leads to a lot of diseases and health complications (Campbell, 2015).

Human activities at the Red Sea coastal area of Saudi Arabia have been increases during the last three decades causing different types of contaminants including heavy metals (Nadia et al., 2009). A comparative study on the concentrations of heavy metals in sediments and fish at Jazan - Saudi Arabia reported a higher percentage of heavy metals than those at the city of Beech for industrial activities and wastewater. The weathering of rocks and flash floods through valleys carry heavy metals such as Ni and Cr to coastal areas, leading to increase pollution with heavy metals (Alhababy, 2016).

Golam and Fahad (2017) have been studied the concentration of heavy metals at Jazan, Saudi Arabia, Red Sea coast within water, sediments and white shrimp. They indicated that heavy metals concentration is higher in water than those in sediments and white leg shrimp. Al Bratty et al. (2017) in their study of determining trace metals in drinking water sources at Jazan Area, Saudi Arabia, stated that trace and major elements were found to be below the standard guideline values, except for uranium in some tap water samples.

Alzahrani et al. (2018) assessed the heavy metals in grey mangrove (*Avicennia marina*) and its associated sediments at the Red Sea coast, Saudi Arabia. They stated that mangrove can accumulate heavy metals, notably Cr and Pb. Also sediments within mangrove areas ranged from moderately to heavily contaminate with Cd at Al-Haridhah area, and moderately contaminated with Cd at South Jeddah, Rabigh, Duba, and Jazan waste water treatment station.

Current research identifies types of heavy metals in Wadi Jazan and their concentrations in order to determine their impact on the environment and its natural components. This will cause pollution of not only the Wadi Jazan land, but the tributaries leading from it and the Red Sea coast beyond. The work will also discuss how to avoid the harmful effects of these minerals and rocks on the environment; as well as the economic importance of some analyzed heavy metals.

Materials and methods

The area of study and sampling

The study area was visited several times to conduct field studies, monitor and photograph observations and field relations. Collection and numbering of samples representing the soil and rocks and plotting their places on the topographical map of the study area by using GPS instrument have been done. In each station, a pit of 40 cm

depth was made and the sample taken at three levels. Level one at the ground surface while level two at depth of 20 cm and level three at depth of 40 cm. The three parts of the sample were mixed in one sample representing the location of the station (*Fig. 1*).



Figure 1. Field photographs clarifying sampling pits and GPS usage for determining sample location attitudes

16 samples were selected for the chemical analysis (Due to the limitation in financial coast which specify for chemical analyses). The chemical analysis carried out for about 25 heavy and rare earths elements which include Li, Be, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Ag, Cd, Sn, Cs, Ba, Au, Tl, Pb and U to identify heavy metals and their concentrations in ppm. The analyzed heavy metals divided into certain groups according to the periodic table of elements. These groups include: Basic metals (Such as Al, Ga, Tl and Pb); transition metals (Such as V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ag, Cd, and Au); alkali metals (Such as Li, Rb and Cs); alkaline earth metals (Such as Be, Se and Ba); semi-metals as As; basic metal as Sn; nonmetallic as Se; and actinides as U. It is clear that the transition heavy metals represent the main bulk of analyzed metals.

The analyses have been done at King Khalid University, Department of Chemistry-Saudi Arabia by using Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). Argon 99.999% - AH and ICP/ICP-MS standard solution of the 25 analysed elements were used. Microwave Digestion System (Anton Par Multiwave ECO) and (Hydrofluoric, Nitric and Hydrochloric acids and Cyclohexanone ACS reagent 99.0%) were used. Where all vessels have been cleaned with deionized water and 1% HNO₃. 0.2 g has been taken from each sample. The following acids (Reagents) were added to each sample: 1 ml of HF (Conc.), 1.5 ml of HNO₃ (Conc.) and 4.5 ml of HCl (Conc.). Then all samples have been digested using the following conditions: Power (800 W), total time (60 min) and temperature (240 °C). Each sample was repeated 3 times. Blank sample was prepared and spike sample as well. The end result of each metal analysis is considered the mean parameter of the three measured values of the same metal in each sample. Standard Deviation was also measured at every time from the three analysed values of each metal, and then the standard deviation mean was calculated for each metal analysis.

Geographical and geological setting

The studied Wadi Jazan area is located at the south west corner of Saudi Arabia on Red Sea coast. Investigated samples were collected during the field work at academic year 2017/2018, in addition some geological and geomorphological characters of the investigated area have been observed. *Figure 2* shows the satellite image of the investigated area around Wadi Jazan, and the location of the analyzed samples. It is clear from the map that Wadi Jazan up streams came from slightly mountainous areas and the main Wadi Jazan and its delta (downstream) are going towards the Red Sea coast at Jazan City.

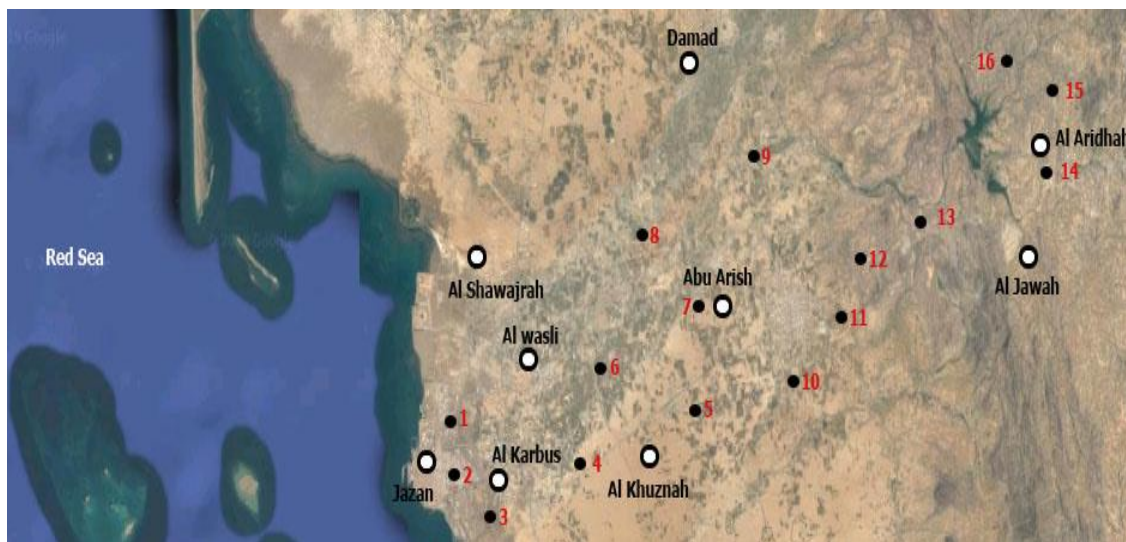


Figure 2. *Satellite image map of Wadi Jazan area, its tributaries, main cities (o) and locations of the analyzed samples (●)*

The investigated area mostly covered by alluvial and compact sediments of recent ages. In some areas near by the Wadi Jazan Dam Lake a volcanic lava flow rocks are present. Upon going further to the east, nearby Al Ardah, mountainous regions are stand up. To the west of Wadi Jazan Dam Lake, alluvial derived sediments are overlying the lava flow rocks. On the ground surface of this area it is observed the presence of rounded pebbles of different composition, shale and andesite flakes and quartz grains. At Wadi Sabiya and its tributaries there are a floodplain sediments of lower relief than its surrounded landscape rocks. These floodplain sediments were covered or capped by a lava flow rocks due to volcanic eruptions (Dabbagh, 1984).

One of the most important field observation at the study area is the presence of wadi floodplain sediments located under the lava flows of volcanic eruption which have been dated locally to 0.8 ± 0.3 mya, K/Ar age dating method (Dabbagh, 1984). There is a possibility to found in Wadi Jazan and its tributaries stratified old relics distributed at different places (Deves et al., 2013). A large numbers of old runes and relics were recovered on the surface of the lava flow on both sides of some tributaries of Wadi Jazan and commonly seen at the base of the quarry sections and represent different historical periods (Inglis, 2014).

Results

Data analysis

Chemical analyses have been done for 16 selected samples from Wadi Jazan area. The selection based on homogenous geographic distribution of samples at Wadi Jazan area and taking in consideration the field observations and surface features examination of mineral grains by using hand lens (10 X magnification). The chemical analyses have been done at King Khalid University, Department of Chemistry-Saudi Arabia by using Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). 25 heavy metals were analyzed in each sample and *Table 1a* shows the chemical analyses of these heavy metals.

In general *Table 1a* delineated that there is richness in the concentration of heavy metals at Wadi Jazan area, in addition to the presence of some concentrations of precious metals such as gold and silver, and the presence of uranium as a radioactive mineral. *Table 1b* provides more comparison between the concentration of analyzed heavy metals in all investigated samples and locations. It shows the average range and the means of analyzed heavy metals concentrations at Wadi Jazan, in addition to the richest areas by heavy metal concentration. For examples: Cadmium (Cd) has an average concentration of 8.98 – 32.97 mg/kg and 20.97 mg/kg as a mean; the richest area is of sample no. 7. Nickel (Ni) ranges from 11.94 to 85.38 mg/kg with average of 48.66 mg/kg, and the richest area is of sample no. 11. Copper (Cu) occurs in-between 12.73 to 132.97 mg/kg and its mean is 72.85 mg/kg; the richest area is of sample No. 15. Lead (Pb) ranges from 6.79 to 32.03 mg/kg with a mean of 19.41 mg/kg; sample no. 7 is considered the richest area. Chromium (Cr) has a range of 23.3 – 131.15 mg/kg and 77.22 mg/kg as a mean; sample no. 16 is the richest area. For uranium (U), the range in-between 0.45 to 23.25 mg/kg and the mean is 11.85 mg/kg while area no. 7 is considered the richest area by uranium. From the data presented in *Table 1b*, it seems that sample no. 7 is the richest sample, of the studied 16 samples, by 9 different heavy metals (Pb, Rb, Sr, As, Se, Tl, Ag, Au and U). This of course will put a great attention on this location at Wadi Jazan (Around Abu Arish City) which will consider as the most polluted area by some harmful heavy metals such as Pb and U. Area of sample no. 11 (also nearby Abu Arish City) is also considered the second polluted locality as it is the richest area by 5 types of heavy metals (Ni, Co, Mn, Be and Ga). One of the most important observation is the more concentrations of heavy metals in areas located mainly nearby the Wadi Jazan upstream (Samples no. 11, 12, 14, 15, and 16), and heavy metal concentrations slightly became lower in areas nearby Wadi Jazan downstream (Samples no 1, 2, 3, 4, 5 and 6). This may explain that the main source of Wadi Jazan heavy metals might be the weathered sedimentary and volcanic rocks that mainly located at Wadi Jazan upstream tributaries. Rains and floods leached these heavy metals and transfer them along through Wadi Jazan to the Red Sea coast. Except the location of samples no 7 and 11 (Around Abu Arish City), which may have additional sources of heavy metals due to human activities in this area (agriculture and industries). *Figure 3* represents histograms for some heavy metals, such as Al, Be, Li and Cr, to show the variation in its concentrations along all analyzed samples.

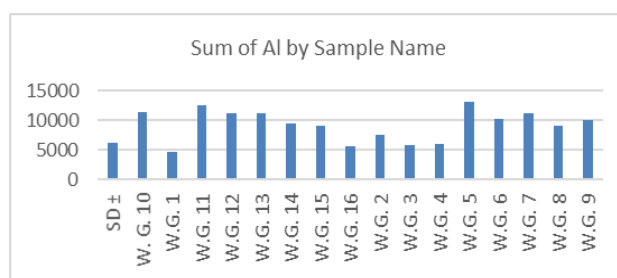
Comparing current data with world permissible levels, general heavy metals characteristics background and the impact of heavy metal contamination of soils will help to understand the impact of heavy metal contamination of soil at Wadi Jazan.

Table 1a. Chemical analyses (mg/kg or ppm) of heavy and rare earth metals of the studied samples (W.G. = Wadi Jazan, SD = standard deviation)

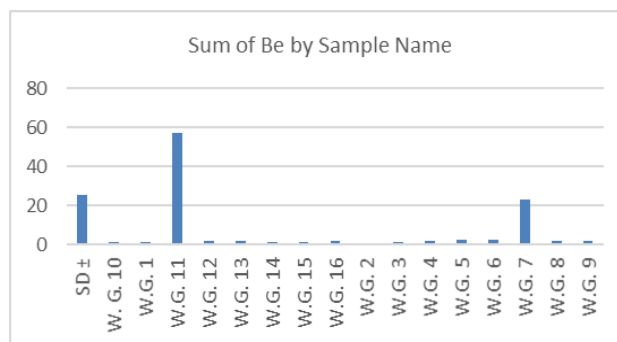
Sample No	Li	Be	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	As	Se	Rb	Sr	Ag	Cd	Sn	Cs	Ba	Au	Tl	Pb	U
W.G. 1	6.65	1.11	4580.06	74.23	79.7	413.84	18197.38	7086.99	38.17	30.06	71.79	39.28	4.36	1.76	6.62	214.82	19.57	11.25	1.76	0.26	967.33	0.59	226.54	14.92	0.88
SD ±	1.81	1.21	105.86	0.64	1.64	2.27	75.75	73.07	1.12	0.42	1.46	0.41	0.13	0.15	0.31	6.17	0.77	0.23	0.14	0.03	27.98	0.08	1.02	0.97	0.03
W.G. 2	4.77	0.59	7456.47	80.42	38.09	461.39	16479.68	6806.88	12.77	19.46	52.59	33.66	3.2	1.72	4.37	84.46	11.27	11.92	1.36	0.43	582.31	0.47	475.88	11.11	0.56
SD ±	0.59	0.88	233.38	0.21	1.24	6.88	435.57	33.97	0.39	0.41	13.04	0.59	0.95	0.18	0.19	3.85	1.12	0.32	0.05	0.01	31.69	0.06	4.93	0.11	0.01
W.G. 3	3.67	1.17	5834.61	74.18	23.3	368.85	11877.4	5367.14	11.94	14.26	41.43	23.15	3.64	1.75	6.8	123.12	6.41	12.04	1.46	0.43	754.71	0.37	283.61	11.89	0.68
SD ±	1.25	0.74	930.38	1.18	0.6	7.18	21.71	32.99	0.24	0.21	0.95	0.37	0.06	0.12	0.45	4.74	0.43	0.49	0.07	0.04	15.33	0.07	7.61	0.14	0.01
W.G. 4	3.31	1.62	5942.86	110.33	90.01	668.12	27814.62	13194.14	64.46	39.74	66.05	27.03	3.27	1.62	3.08	131.85	13.73	11.66	1.73	0.44	542.65	2.25	642.69	16.58	0.68
SD ±	0.52	1.08	110.56	0.77	1.5	3.93	121.64	1221.91	1.5	0.38	1.88	0.35	0.03	0.15	0.26	6.33	0.25	0.48	0.06	0.02	10.52	0.04	7.75	0.22	0.02
W.G. 5	7.25	2.34	13149.02	98.86	47.76	509.77	29187.03	15578.13	15.63	27	39.26	35.43	3.83	2.22	6.88	101.45	10.64	11.49	1.84	0.42	1347.52	1.33	779.38	16.42	0.76
SD ±	1.35	0.65	597.27	0.94	0.35	8.21	137.2	641.61	0.54	0.42	1.13	0.99	0.13	0.2	0.39	0.46	0.6	0.36	0.1	0.02	24.71	0.13	25.98	0.15	0.02
W.G. 6	5.77	2.37	10174.13	103.23	57.94	597.88	24053.7	10770.64	17.41	12.73	55.89	30.62	4.27	1.73	6.35	75.4	5.21	11.07	1.71	0.61	2444.49	1.37	348.07	9.3	0.97
SD ±	2.37	1.16	890.4	1.23	1.05	11.82	128.98	738.03	0.39	0.26	0.32	1.25	0.17	0.16	0.23	1.63	0.31	0.25	0.09	0.03	177.12	0.1	0.04	0.11	0.42
W.G. 7	29.82	22.93	11249.09	144.59	95.31	686.71	21311.04	11786.54	52.54	56.23	102.18	64.95	25.92	23.75	26.93	96.14	46.41	32.97	2.05	21.57	727.09	2053.01	982.08	32.03	23.25
SD ±	5.05	3.68	189.78	1.03	1.52	9.05	267.42	599.55	1.36	0.71	2.69	0.42	0.11	0.12	0.5	1.48	0.47	0.18	0.12	0.01	13.17	0.09	15.28	0.15	0.03
W.G. 8	4.21	1.72	9121.44	112.2	56.23	505.18	23005.42	9454.87	22.86	26.64	63.48	63.46	6.02	2.86	4.78	79.74	9.93	10.57	1.82	0.46	771.51	0.8	441.75	9.12	0.81
SD ±	1.95	2.29	279.53	1.61	1.93	9.3	124.97	37.67	0.49	0.99	1.21	0.89	0.09	0.22	0.14	1.59	0.07	0.19	0.09	0.02	54.61	0.09	12.14	0.1	0.02
W.G. 9	7.42	1.98	10044.48	95.48	65.05	505.46	20.8	8.99	18.32	23.12	61.72	69.63	3.18	2.23	4.5	70.11	2.41	8.98	1.83	0.26	650.81	0.87	115.62	10.35	0.89
SD ±	2.24	1.92	72.37	2.02	1.36	4.53	81.95	43.15	0.51	0.6	0.6	1.24	0.07	0.21	0.43	4.01	0.15	0.15	0.12	0.02	24.58	0.11	2.12	0.25	0.01
W.G. 10	5.74	1.15	11418.38	86.15	52.88	462.14	18432.85	7512.95	21.77	23.97	69.29	69.63	2.57	1.87	5.59	55.92	4.16	11.64	1.67	0.33	597.16	0.54	628.85	13.61	1.44
SD ±	1.79	0.83	490.24	1.26	2.13	3.3	141.44	167.18	0.27	0.31	2.11	0.96	0.07	0.23	0.26	3.62	0.26	0.54	0.24	0.02	14.76	0.06	51.12	0.15	0.05
W.G. 11	8.07	57.24	12449.26	183.57	106.22	811.58	39325.02	15434.45	85.38	60.2	104.34	89.19	5.35	2.93	4.34	53.92	6.7	11.35	2.63	0.45	1253.98	0.59	503.8	16.66	1.09
SD ±	4.26	2.69	294.63	2.35	2.52	15.14	182.95	562.81	2.16	1.2	1.88	1.74	0.15	0.16	0.07	1.36	0.32	0.22	0.19	0.02	31.64	0.08	26.58	0.32	0.05
W.G. 12	5.8	1.75	11262.12	149.12	87.35	729.78	47601.44	12278.77	33.61	48.09	91.99	47.38	6.55	4.54	2.94	9.05	41.15	10.13	1.75	0.47	1000.97	1	732.01	12.82	0.55
SD ±	3.42	1.78	334.2	3.47	1.02	28.18	333.72	153.45	0.63	1.33	1.64	1.72	0.24	0.32	0.24	1.06	0.72	0.62	0.06	0.04	42.92	0.06	64.33	0.24	0.04
W.G. 13	7.36	1.44	11235.5	85.55	38.37	355.59	16755.41	8412.82	11.69	23.85	61.16	36.27	2.68	1.97	13.31	67.29	8.98	11.37	2.05	2.23	1007.6	0.66	139.93	12.05	0.45
SD ±	4.18	1.3	1374.81	1.59	0.48	14.76	112.57	99.89	0.38	0.54	1.14	0.97	0.09	0.22	0.19	1.02	0.7	0.77	0.19	0.06	31.5	0.07	0.03	0.15	0.01
W.G. 14	46.64	1.41	9467.42	97.93	52.62	573.49	25821.97	8179.59	16.3	49.47	64.66	35.45	2.35	1.95	26.68	69.89	6.68	11.72	1.62	6.95	698.73	3.14	488.15	11.27	0.61
SD ±	5.3	1.89	89.06	2.23	1.57	4.99	44.66	176.63	0.73	0.63	1.22	1.48	0.17	0.28	2.03	2.23	0.44	0.39	0.07	0.11	35.49	0.19	11.54	0.23	0.03
W.G. 15	6.83	0.91	9018.99	97.09	34.34	704.53	22440.49	8299.29	18.04	132.97	112.34	44.23	3.54	2.2	10.4	54.74	3.37	11.34	1.78	1.52	999.39	0.88	218.6	9.51	0.6
SD ±	3.05	1.46	165.76	1.02	0.77	8.53	139.4	371.66	0.51	3.12	1.76	1.31	0.07	0.19	0.77	2.02	0.07	0.3	0.25	0.06	40.63	0.08	4.93	0.09	0.04
W.G. 16	7.68	1.91	5665.41	169.89	131.15	763.04	40590.34	15241.46	84.77	73.92	81.76	47.4	7.46	3.79	0.92	15.29	8.03	10.02	2.8	0.4	146.44	0.53	708	6.79	1.3
SD ±	2.97	1.61	102.37	1.4	2.33	14.46	2224.39	120.53	0.97	1.06	1.5	1.46	0.18	0.27	0.1	0.6	0.05	0.06	0.21	0.01	37.87	0.05	0.01	0.2	0.05

Table 1b. Comparison between range, mean and the richest concentrations of analyzed heavy metals at Wadi Jazan

Heavy metal (mg/kg)	Range at Wadi Jazan (mg/kg)	Mean at Wadi Jazan (mg/kg)	The richest area (Sample No.)
Li	3.67 – 46.64	24.15	14
Be	0.59 – 57.24	28.91	11
Al	4580.06 – 13149.02	8864.54	5
V	74.18 – 169.89	122.03	16
Cr	23.3 – 131.15	77.22	16
Mn	355.59 – 811.58	583.58	11
Fe	20.8 – 47601.44	23811.12	12
Co	8.99 – 15434.45	7721.72	11
Ni	11.94 – 85.38	48.66	11
Cu	12.73 – 132.97	72.85	15
Zn	39.26 – 112.34	75.80	15
Ga	23.15 – 89.19	56.17	11
As	2.35 – 25.92	14.13	7
Se	1.62 – 23.75	12.68	7
Rb	0.92 – 26.93	13.92	7
Sr	15.29 – 214.82	115.05	1
Ag	2.41 – 46.41	24.41	7
Cd	8.98 – 32.97	20.97	7
Sn	1.36 – 2.80	2.08	16
Cs	0.26 – 6.95	3.61	14
Ba	146.44 – 2444.49	1295.46	6
Au	0.37 – 2053.01	1026.69	7
Tl	115.62 – 982.08	548.85	7
Pb	6.79 – 32.03	19.41	7
U	0.45 – 23.25	11.85	7



a



b

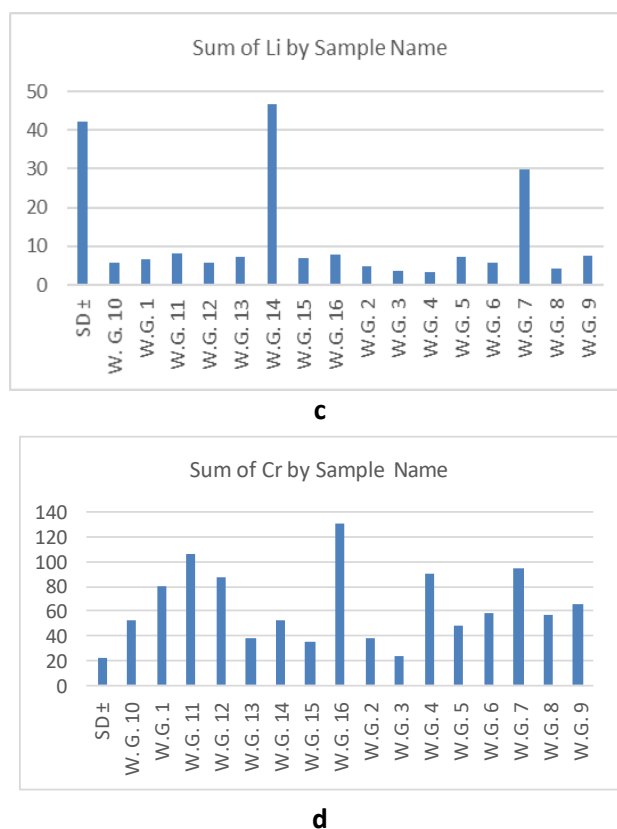


Figure 3. Histograms showing the concentrations of some selected heavy metals at different locations of the analyzed samples at the study area: (a) Shows that sample no 5 is the richest in Al, (b) Delineates that sample no. 11 is the richest in Be, (c) Shows that sample no. 14 considered the richest in Li, while (d) Indicate that sample no 16 is the richest in Cr

Worldwide characteristics of heavy metal contamination of soils

1. Wide distribution: Economy and society development makes heavy metal contamination a serious threat to every country. In the world's top ten environmental events, two events have related to heavy metal contamination (Yang and Sun, 2009).
2. Strong concealment: As a result of colorless and odorless of heavy metal contamination, so it is difficult to be noticed. Nevertheless, when environmental conditions have changed heavy metals in the soil may be activated and cause serious ecological damage. So heavy metal contamination is usually chemical time bombs (Wood, 1974).
3. Difficulty of treatment: Air and water pollution problems can be solved by dilution and self-purification after controlling the sources of pollution. However, it is difficult to apply these techniques to get soils improved. Some soils contaminated by heavy metals could take one or two hundred years to be remediated (Wood, 1974). Therefore, remediation of heavy metal contamination in soils is expensively and the remediation cycle is relatively long.
4. Complex heavy metal contamination: Soil contamination in the past was mainly caused by a single heavy metal. However, in recent years more cases

are found to be caused by a variety of heavy metals that led to compose contamination by heavy metal complexes (Zhou, 1995).

Common sources of heavy metals

Heavy metals in soils have different sources which include atmospheric deposition, sewage irrigation, industrial solid waste, mining activities, use of pesticides and fertilizers (Zhang et al., 2011).

1. Atmosphere to soils pathway: Heavy metals in the atmosphere are mainly from gas and dust produced by energy, transport, metallurgy and production of construction materials. The amount of heavy metals which went into the soil through natural deposition and raining sedimentation are related to the level of development of heavy industry, the city's population density, land utilization and traffic level. Soil contamination became to be heavier as closing to the city (Chen, 2002).
2. Sewage to soils pathway: Heavy metals are brought to the soil by irrigative sewage and are fixed in the soil in different ways. It causes heavy metals (Hg, Cd, Pb, Cr, etc.) to continually accumulate in the soil year by year.
3. Solid wastes to soils pathway: Mining and industrial solid waste contamination is the most common. When these wastes are piled or governed, heavy metals move easily due to the facilitation of sunlight, raining and washing leading to spread to the surrounding water and soils (Ding, 2000).
4. Agricultural supplies to soils pathway: Fertilizers, pesticides and mulch are important agricultural inputs for agricultural production (Zhang and Zhang, 2007; Zhang et al., 2011). Heavy metals are the most reported pollutants in fertilizers and the long time using of these products has resulted in the heavy metal contamination of soils (Arao et al., 2010).

Results compared with international permissible contamination

The maximum permissible heavy metal concentration in soil designated by the world health organization (WHO) is tabulated in *Table 2*.

Table 2. Maximum allowed concentration limits of some toxic metals in soil (mg/kg or ppm). (WHO, 1996)

Toxic metal	WHO maximum allowed limits (ppm)
Nickel (Ni)	80
Copper (Cu)	30
Cadmium (Cd)	3
Chromium (Cr)	100
Lead (Pb)	100
Zinc (Zn)	300

When comparing analyzed data of heavy metals in Wadi Jazan soils (*Table 1*) with those of WHO (1996) which presented in (*Table 2*) we found that: For Ni, only samples 11 and 16 are highly polluted and toxic by Ni. Samples 4, 7, 11, 12, 14, 15 and 16 at Wadi Jazan are highly polluted by Cu. For Cr only samples 11 and 16 are the most toxic, while for Pb and Zn all analyzed samples at Wadi Jazan are not polluted. The

most extremely soil pollution at Wadi Jazan is by Cd, where all analyzed samples have higher concentration than the maximum permissible concentration by WHO. One of the most important observations from this comparison is the high toxicity of samples 11 and 16 by different heavy metals that should be taken in consideration for its environmental impact.

Table 3 presents the results of some trace and heavy metals concentration levels (Range and mean) in soils of Wadi Jazan, compared with international standard permissible levels in mg/kg (Hong, et al., 2014).

Table 3. Mean concentration of investigated Wadi Jazan heavy metals compared to international standard limits of heavy metals in soil in mg/kg (Hong et al., 2014). EU = European Union Standard, USA = United State of America Standard, UK = United Kingdom standard

Heavy metal (mg/kg)	Range at Wadi Jazan	Mean at Wadi Jazan	EU standard (mg/kg)	UK standard (mg/kg)	USA standard (mg/kg)
Fe	20.8 - 47601.44	23811.12	-	-	-
Zn	39.26 – 104.34	71.8	300	200	200 - 300
Mn	355.59 – 811.58	583.58	-	-	-
Cu	12.73 – 132.97	72.85	140	63	80 – 200
Cd	8.98 – 32.97	20.97	3	1.4	3
Cr	34.34 – 131.15	82.74	180	6.4	400
Pb	6.79 - 32.03	19.41	300	70	300

The compared results indicate significant variation in heavy metal levels in Wadi Jazan soil with respect to international levels. At all sites higher concentrations of Cd were observed than those compared world permissible Cd concentration. However concentrations of Wadi Jazan Zn, Cu, Cr and Pb heavy metals are lower than the compared international levels.

Heavy metals are specified into three classes of hazard according to (Vodyanitskii, 2016): The first (high-hazard) class includes As, Cd, Hg, Se, Pb, and Zn; the second (medium-hazard) class contains B, Co, Ni, Mo, Cu, Sb, and Cr; and the third (low-hazard) class encompasses Ba, V, W, Mn, and Sr. So it is possible to generalize that the total contamination will apparently be more hazardous in the case when the most toxic elements belonging to the first group are accumulated in soils rather than the low-toxic elements of the third group. Our analyzed data on Table 1 indicates the presence of the three hazard classes of heavy metals, which led to take the environmental impact of these heavy metals concentration at Wadi Jazan very seriously now.

Discussion

Living organisms require various amounts of heavy metals such as iron, cobalt, copper, manganese, molybdenum, zinc and selenium. Where the consumption of these minerals is necessary and important to activate the metabolism of the body of these organisms. However, the consumption of large amounts (high concentrations) is harmful and even toxic and results in so-called heavy metal poisoning (Bolzan, 2014). Minerals account for 45% of the human body's weight, and most are concentrated in the skeleton. The dangerous of heavy metals comes from their bioaccumulation within the

human body faster than their degradation through the metabolism or output. The impact of heavy metals is due to the large distribution of biological agents among the various environmental components (water, air, soil) as well as among the components of the food chain. For example, rainwater works to dissolve rocks and raw minerals that are transported to currents and rivers to be distributed among the various environmental components and are bio concentration among organisms and then reach the food chain (Bharti, 2012).

Concentration of heavy metals, whether high or low, depends on several things (Jiwan et al., 2011) including: 1- If these minerals are found in water (Water pollution), their concentration is controlled by temperature, salinity, water waves, density, and the presence of coral reefs. 2- If these minerals are found in the air (Air pollution), they depend on air components in the environment such as carbon dioxide, nitrogen dioxide, temperature, and humidity. 3- If these minerals are present in the soil (Soil pollution), there are several factors that lead to increased concentration (Soil pollution), the presence of binding elements such as zinc to connect cadmium, as well as bacterial and biological groups, and concentration of organic gases such as methane and ethane. 4- If these minerals exist in living organisms (Pollution in living organisms), they are controlled by many factors such as: the movement of enzymes and the type of the organism. Some organisms have found quick absorption of contaminants due to the presence of help factors, and some animals reject heavy elements and contaminants due to the presence of other help factors as well. 5- It has also been scientifically proven that the concentration of minerals in different environments depends on the type of the pollutant and the state of the pollutant (gas, liquid, or solid).

Impact of heavy metal contamination of soils

1. Impact on soil microorganisms and enzymatic activity

Soil pollution can be caused by various pollutants, but heavy metals (Specially Cu, Ni, Cd, Zn, Cr and Pb) considered the main source (Hinojosa et al., 2004). Soil content from organic matter, clay minerals and P^H value have a direct influence on the effects of heavy metals on the soil biochemical characteristics of organisms (Speira et al., 1999). The toxic effect of heavy metals on soil organisms is to disrupt their biological processes, reduce their activity and their numbers. Some heavy metals cause disturbances on the enzyme activities and their chemical effects in the soil by different ways. Cd has more toxic effect to enzymes than Pb due to its higher ability for movements and lower adhesion with soil granules (Karaca et al., 2010). Our investigated samples at Wadi Jazan (*Table 1*) proved the presence of some heavy metals by considerable concentrations that caused soil pollution of Wadi Jazan area. These metals are mostly represented by Cu, Ni, Cd, Zn, Cr and Pb. On the other hand, one of the most important harmful mineral on the soil and all environments is U, which all our analyzed samples indicate its appearance in all over Wadi Jazan soil.

2. Impact on the plants

Plants growth has a physiological relationship with metals content of soil. Some heavy metals as As, Cd, Hg, Pb and Se are not provide any known physiological role in plants, but Co, Cu, Fe, Mn, Mo, Ni and Zn are considered a required metals for normal plants growth and activation of its metabolism processes. When the concentration of these elements increased over the suitable needed amount of plants growth, they

become poisoning for plants and its final products (Rascio and Izzo, 2011). According to plant species and its ability for absorbing metals, the accumulation of heavy metals in plants occurs (Khan et al., 2008). In Florida, it was found that if the copper content in soil was more than 50 mg/ kg, it would affect citrus seedlings; if soil copper content reached 200 mg/ kg, wheat would wither (Zhang et al., 1989). This mean that soil of samples 15 (Cu = 132 mg/kg) and 16 (Cu = 73 mg/kg) at wadi Jazan are considered the worst places that have direct poisonous impact on plants. Plants absorption of heavy metals and subsequently its entering to the food chain is consider a harmful effect to animals and human health (Sprynskyy et al., 2007). Heavy metals absorption by plants roots is the main reason of heavy metals entrance to the food chain (Jordao et al., 2006). Presence of high concentrations of some heavy metals in Wadi Jazan area (*Table 1*) such as Cd, Zn, Cr, Mn, Cu, Ni, Pb, U and others may indicate that the growing plants, vegetation and trees at Wadi Jazan could have the chance for pollution by these heavy metals. Further future studies are needed to characterize the effect of high concentrations of some heavy metals in soil of Wadi Jazan area on plants, and to see to what extent these heavy metals were entered to the food chain.

3. Impact on the animals and fish

Terrestrial animals are mostly growing by consumption of water and plants during their daily life. High concentrations of heavy metals at Wadi Jazan soil and ground (*Table 1*) may cause the entrance of these heavy metals to the ground water and plants, hence the transfer to the food chain of animals. Of course these heavy metals cause danger effect on animal health and their growing. Not only this, but also will accumulated in the tissues of these animals and will transfer to human during the food chain.

In aquatic environment heavy metals are toxic even though when they present by small amounts. Heavy metals stand strongly against bacterial alteration and remain always in the marine (Woo et al., 2008). Heavy metals in aquatic environment commonly associated with small particles which precipitated with sediments. Recent surface sediments is considered the main tank of different minerals including heavy ones. Upon accumulation of heavy metals in aquatic microorganisms then fish, the transportation of these heavy metals to higher classes food chain is possible. Humans and other carnivores which represent the food chain top obtained their heavy metals indirectly from marine environments through the food. Fish consider the main factor for transferring heavy metals to higher classes food chain (Ayandiran et al., 2009). Taking into consideration the presence of different types of heavy metals at Wadi Jazan soil and its tributaries (*Table 1*). There is ability of rain water and runoff to transfer these heavy metals to the ground water and the Red Sea aquatic environment.

4. Impact on humans

The transportation of heavy metals from soil to plants, pastoral animals and fish, especially soil of high concentration in heavy metals led to human's health risk. Also taking into consideration the implications of food-chain that contaminated by heavy metals, it is intrinsic to conclude that food-chain considered the main route for humans exposure. Of course when heavy metals are not metabolized by human body they will accumulate in soft tissues causing different diseases. For example, Cd is a toxic heavy metal and has 8.65 specific gravity which is considered greater than water nearly by 8

times. The liver, kidneys, lungs, bones and brain are the main target organs for Cd toxicity (Sobha et al., 2007). Cd may damage the metabolism of calcium, which will cause calcium deficiency and result in cartilage disease and bone fractures, etc. Agency for Toxic Substances Management Committee has listed Cd as the sixth most toxic substance that damages human health. Also the toxic clinical characteristics of Zn mainly referred as vomiting, diarrhea, bloody urine, liver and kidney failure and anemia (Durube et al., 2007). Despite Cu is considered as an essential element for mammalian nutrition where it is activate electrons movements between enzymes, but when they exposed to high Cu levels a number of harmful health problems could be happened (Stern et al., 2007). Pb affects and damages many of the body organs and systems, such as kidney, liver, reproductive system, nervous system, urinary system, immune system and the basic physiological processes of cells and gene expression. Ni is tumor promoting factor, whose carcinogenesis effect has attracted global concerns. Workers who are in close contact with the nickel powder are more likely to suffer from respiratory cancer, and the content of Ni in the environment is positively correlated with nasopharyngeal carcinoma (Chen, 2011).

According to the previous discussion and explanation about the effect of heavy metals on human, it is possible to reflect to what extent the presence and concentrations of heavy metals (*Table 1*) at Wadi Jazan area have a direct effect on the health of human populations and the environment in general. The source of these heavy metals at Wadi Jazan is most probably the different types of igneous and sedimentary rocks that located at the upper streams of the Wadi. The product of weathering processes of these rocks led to the release of their heavy metals content, and as a result of water runoff along the different wadi tributaries these heavy metals transfer to everywhere at Wadi Jazan and coastal areas. It could be some other additional sources such as industrial activities and the used compost in agriculture activities along the wadi.

From an economic point of view, *Table 1* shows the presence of some economic minerals such as Au, Ag, U, Li and other rare earth elements. In the future the precious metals such as Au and Ag should be evaluated by further studies at Wadi Jazan area, it could be present by economical values. U and Li are very important minerals (strategic minerals) which could be used in different industries. The present study refers preliminary to its presence, of course it need further detailed studies for make full evaluation and prediction of its reserve at Wadi Jazan area. Other occurred rare earth elements participate in different high tech industries and need further investigations as it wasn't the target of this research.

As a result of heavy metals accumulation in food chains and its harmful effect to living organisms a demand was increased around the world to technology of heavy metals separation and purification. Heavy metals can reach to water bodies due to agricultural runoff, industrial activities and applications. There are different technologies that can be used for heavy metals removal from water. These remediation technologies include: Precipitation and coagulation, ion exchange, membrane filtration, bioremediation, heterogeneous photo catalysts and adsorption (Gautam et al., 2015).

Remediation of heavy metal contaminated soils

1. Engineering remediation

Engineering remediation refers to using physical or chemical methods to control heavy metal contamination of soils.

a) Replacement of contaminated soil, soil removal and soil isolation:

Replacement of contaminated soil means adding large amount of clean soil to cover on the surface of the contaminated soil. Soil removal refers to remove the contaminated soil and renew it with the clean soil. Soil isolation means that to isolate the contaminated soil from the uncontaminated soil, but to completely remedy it still needs other auxiliary engineering measures (Zheng et al., 2002). All of these methods will cost large amount of manpower and material resources, so they can only be applied to small area of soils.

b) Electro kinetic remediation:

Soil electro kinetic remediation is a new economically effective technology. The principle is that the DC-voltage is applied to form the electric field gradient on both sides of the electrolytic tank which contains the contaminated soil. Through the way of electro-migration, electric seepage or electrophoresis, and thus reduce the contamination. The method performs well in the soil with low permeability (Hanson et al., 1992).

c) Soil leaching:

Soil leaching is to wash the heavy metal contaminated soil with specific reagents and thus remove the heavy metal complex and soluble ions adsorbed on the solid phase particles. By using this method, heavy metals are separated from the soil, and heavy metals are then recycled from extracting solution.

d) Adsorption:

Adsorption method is based on the fact that almost all heavy metal ions can be fixed and adsorbed by clay mineral (bentonite, zeolite, etc.), a steel slag, furnace slag, etc. (Wang and Zhou, 2004).

The most suitable techniques for Wadi Jazan are replacement of contaminated soil, soil removal, soil isolation and adsorption because of the small area of soils that have metal toxicity, and also due to the presence of some local resources (Such as used bentonite clay mineral in adsorption technique).

2. Bioremediation

a) Phytoremediation:

Using plants and their coexisting microbial system to remove heavy metals is a new technology. The key of the method is to find the suitable plants with strong ability for heavy metal accumulation and tolerance. Now more than 400 species of such plants have been found in the world, and most of them belong to Cruciferae, including the genus Brassica, Alyssums, and Thlaspi (Xin et al., 2003).

b) Microbial remediation:

Microbial remediation refers to using some microorganisms to perform the absorption, precipitation, oxidation and reduction of heavy metals in the soil. Siegel et al. (1986) found that fungi could secrete amino acids, organic acids and other

metabolites to dissolve heavy metals and the mineral containing heavy metals. Fred et al. (2001) reported that the fungi, *Gomus intraradices*, may improve the tolerance and absorption of sunflower to Cr.

c) Animal remediation:

Some animals living in the soil (maggots, earthworms, etc.) can take heavy metals in the soil. Wang et al. (2007) proved that when the concentration of Cu was low in the soil, the activities and secretion of earthworms could promote the absorption of Cu by ryegrass.

Phytoremediation technique could be considered most more effective to use at Wadi Jazan due to the suitability of the environmental conditions at Wadi Jazan for growing some plants which used in removing heavy metals depending on its microbial system (Such as Cruciferae, including the genus *Brassica*, *Alyssums*, and *Thlaspi*).

Conclusion

Sediments of Wadi Jazan area contaminated by different types of heavy metals and by different concentrations. These metals include Li, Be, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Ag, Cd, Sn, Cs, Ba, Au, Tl, Pb and U. Investigated heavy metals has a direct and indirect harmful environmental impact on soil, plants, terrestrial animals, aquatic environment and human health. Comparing analyzed heavy metals with those permissible by WHO indicate that: For Ni, only samples 11 and 16 are highly polluted and toxic by Ni. Samples 4, 7, 11, 12, 14, 15 and 16 at Wadi Jazan are highly polluted by Cu. For Cr only samples 11 and 16 are the most toxic, while for Pb and Zn all analyzed samples at Wadi Jazan are not polluted. The most extremely soil pollution at Wadi Jazan is by Cd, where all analyzed samples have higher concentration than the maximum permissible concentration by WHO. One of the most important observations is the high toxicity of samples 11 and 16 by different heavy metals that should be taken in consideration for its intensive environmental impact.

Heavy metals concentrations along Wadi Jazan indicate that the most polluted area is located around Abu Arish City. The main source of Wadi Jazan heavy metals might be the weathered sedimentary and igneous rocks that located at Wadi Jazan upstream tributaries. Rains and floods leached these heavy metals and transfer them along through Wadi Jazan to the Red Sea coast. Except the location of Abu Arish City which may have additional sources of heavy metals due to human activities in agriculture and industries.

The present study concluded the suitability of some recent techniques for soil remediation at Wadi Jazan, such as engineering remediation (Replacement of contaminated soil, soil removal, soil isolation and adsorption) and bioremediation (Phytoremediation). Selected techniques of engineering remediation are considered the most suitable ones for Wadi Jazan because of the small area of soils that have metal toxicity, and also due to the presence of some local resources (Such as used bentonite mineral in adsorption technique). Phytoremediation technique can also use due to the suitability of the environmental conditions at Wadi Jazan for growing some plants that used in removing heavy metals depending on its microbial system (Such as Cruciferae, including the genus *Brassica*, *Alyssums*, and *Thlaspi*).

Current investigation also clarify that some studied heavy metals have economic importance usage (Such as Au, Ag and U), and need further evaluations in the future.

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