

Pollution assessment of arsenic and other selected elements in the groundwater and soil of the Gulf of Aqaba, Saudi Arabia

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Abstract Forty-six soil and groundwater samples were collected from the agricultural farms of the Gulf of Aqaba coast. Additionally, 24 granitic and marine sedimentary rock samples were collected from the study area. The collected samples were analyzed for As, Al, Au, B, Ba, Be, Fe, Sb, Se, Sn, Ti, and V using inductively coupled plasma mass spectrometry. Levels of the studied metals in the groundwater samples lie within the acceptable limits of the World Health Organization (WHO). The rock samples exhibit a significant variation in mean metal content from one rock type to another. Concentrations of As and B in the soil samples were determined to be higher than those of Canadian Soil Quality Guidelines (CSQG) and were primarily due to agricultural and seawater inputs. Chemical weathering of various rock units also plays a significant role. The calculations of geoaccumulation index are found to be more reliable than of those of enrichment factor for Arsenic contamination levels assessment. The study area is not significantly affected by As contamination. The correlation coefficient analysis results for the soil and groundwater data reveal a variable degree of correlations between As and other metals in the study area.

Keywords Soil · Groundwater · Arsenic · Gulf of Aqaba · Assessment

Introduction

Arsenic (As) is a major global environmental toxicant. The presence of As in high concentrations in water and soil endangers human health. Although drinking water is the main route of As intake into the human body, the food chain can also be another significant route of As uptake, i.e., where people are consuming contaminated crops, vegetables and animals (Tamasi and Cini 2004; Asante et al. 2007; Garcia-Sanchez et al. 2010; Navoni et al. 2014).

Natural weathering of rocks and minerals containing As and anthropogenic sources are possible origins of As in the soil. Anthropogenic sources include mining and smelting activities, the use of arsenical wood preservatives and livestock feed additives, fossil fuel combustion, agricultural practices, industrial activities, and waste disposal (Smith et al. 1998; Garcia-Sanchez and Ayuso 2003; Garelick et al. 2008).

The environmental risk of As is associated with its mobile or bioavailable chemical forms in soil. The dominant inorganic forms of As in natural soil systems are arsenate (As(V)) and arsenite (As(III)), which are present under aerobic and anaerobic conditions, respectively (Asante et al. 2007). Adsorption of As on soil mineral surfaces is a very important process that affects its mobility and fate in the environment, as well as its availability for biological cycling (Tamaki and Frankenberger 1992). Arsenic mobility and bioavailability in soil and aquatic environments are a function of pH, redox potential, the presence and types of adsorbing surfaces, and microbial population (Masscheleyn et al. 1991; McGeehan and Naylor 1994; Dowdle et al. 1996).

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The study area makes part of the Gulf of Aqaba coastal areas where the dominant industries are machine brick, ceramic, and asphalt manufacturing. The main activities of the local community are breeding sheeps, goats and crop production. Since the Saudi authorities are expressing increasing interest in developing similar areas and in setting related sustainable management plans, it deemed necessary to investigate the available natural resources and characterize the available hydrogeological resources. Consequently, decision makers will be able to take a well-informed decisions based on scientific facts. As an initiative to provide part of the necessary information, a research team at the King Saud University (KSU) has launched, in early 2012, an extensive research campaign in the area. Several publications illustrating the findings of this campaign have been published. Batayneh et al. (2012a, b) studied the heavy metals toxicity in the shallow aquifer system in the area. Ghrefat et al. (2013) studied the geochemical and weathering processes that control groundwater composition. Furthermore, Ghrefat et al. (2014) geochemically assess the groundwater contamination by fluoride. The role of existed structural features in determining the characteristics of the hydrogeological resources has been investigated by Elawadi et al. (2013) using geophysical methods. However, no study for evaluating arsenic contamination in the Gulf of Aqaba has been conducted in the area. Specific objectives of the current study are: (1) therefore, to analyse the total concentration and spatial distribution of several metals including As, Al, Au, B, Ba, Be, Fe, Sb, Se, Sn, Ti, and V in the groundwater and soils of the agricultural farms along the Gulf of Aqaba, (2) to carry out a preliminary assessment of the environmental risk associated with arsenic and other metals pollution using enrichment factor (EF) and geoaccumulation index (Igeo), and (3) to determine the inter-relationship between Arsenic and other metals.

Location, geology and hydrogeology of the study area

Location

The Gulf of Aqaba constitutes an eastern arm of the northern tip of the Red Sea. This partially enclosed body of water is connected to the Red Sea by the Strait of Tiran Fig. 1. The Gulf of Aqaba is approximately 180 km long with a maximum width of 25 km. It is located in a zone that has a sub-tropical arid climate, extremely high temperatures and low precipitation. Oceanographic characteristics of this partially enclosed gulf create a unique environment for biodiversity growth.

The area chosen for this study is located along the eastern coast of the Gulf of Aqaba. This coast begins 1 km from the Jordanian border in the northeast and stretches southwest for 50 km towards the Strait of Tiran (Fig. 1). The study area contains groundwater resources used for domestic and agricultural activities. Surface water flow is generally non-existent in the area, but occasional flooding occurs because of heavy rainfalls (Batayneh et al. 2012a).

Hydrogeology

Groundwater in the area occurs in two geologic units: the alluvial deposits of the wadi systems and the clastic coarse members of the Cretaceous-Tertiary sedimentary succession (Mogren et al. 2011; Batayneh et al. 2012b). The alluvial water aquifers are heterogeneous in nature and are made of unconsolidated gravels, sand, clay, clayey sand, and silt. The coarse-grained rock units, which dominate in the upstream areas, decrease in the downstream direction towards the coastal plain. Water levels vary from approximately 60 m above sea level in the headwaters to approximately 10 m above sea level in the coastal plain. Groundwater aquifers primarily recharge from rare, intermittent rainfall events. Most of the surface runoff in the surrounding wadies does not reach the sea due to high evaporation and water percolation into the ground.

Geologic setting

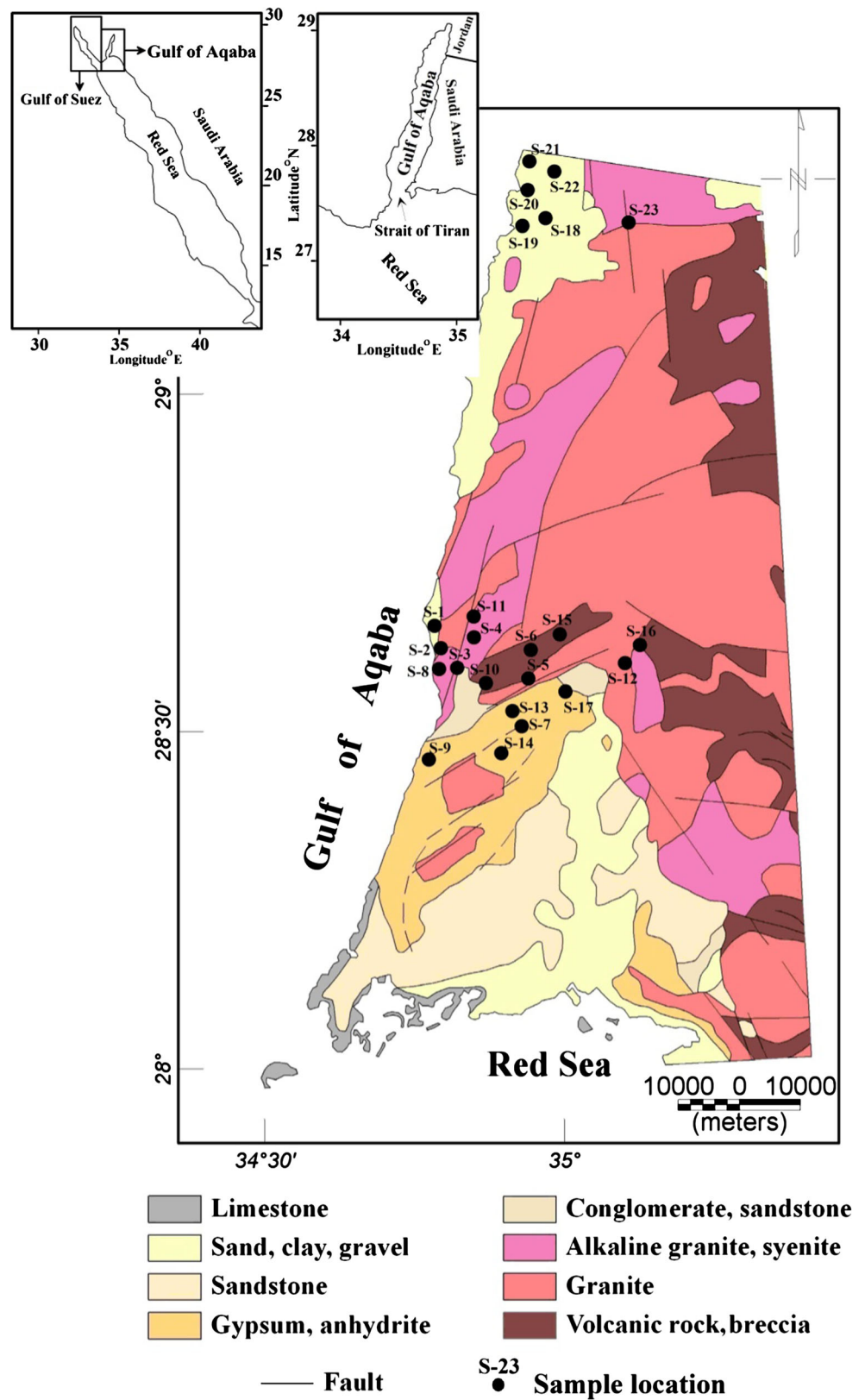
From a geological point of view (Fig. 1), the Late Cretaceous Adaffa Formation (fluvial in origin) is the oldest sedimentary rock unit in the area; it unconformably overlies the Proterozoic basement rocks (Clark 1986; Wyn Hughes and Johnson 2005). The metamorphic basement varies in composition from monzogranite to alkali feldspar granite. The Adaffa Formation is then unconformably overlain by Early Miocene Burqan Formation (deep marine in origin), which in turn is overlain by marine mudstones, carbonates and evaporites of the middle Miocene age. The poorly exposed middle Miocene Mansiyah and middle to upper Miocene Ghawwas formations are made of marine evaporites and shallow to marginal marine sediments, respectively. The youngest rocks in the area are the alluvial sands and gravels of the Late Pliocene Lisan Formation.

Materials and methods

Sampling and analysis

Groundwater samples were collected in March 2012 from twenty-three different wells along the coastal areas of the Gulf of Aqaba, Saudi Arabia. Sampling wells are presented

Fig. 1 Geological map for the Gulf of Aqaba-Red Sea region (modified after Clark 1986). Black circles indicate the groundwater and soil sample locations. The inset maps show the Red Sea, the Gulf of Suez, the Gulf of Aqaba, and the Straits of Tiran



in Fig. 1. Most of wells sampled are privately owned, dug in shallow aquifers and located in relatively close proximity to the east coast, except for well 23 (which accesses a

deep aquifer located approximately 20 km further east of the coast). After purging, samples were collected in 1 l precleaned polyethylene containers. Following collection,

samples were kept refrigerated at 4 °C and transported to a water laboratory for subsequent chemical analyses. In addition to dissolved metals, a variety of physical and chemical parameters were analyzed. The pH, redox potential, and specific conductance (EC, dS m^{-1} at 25 °C) were directly measured in situ using portable field meters. Trace elements were measured with an Inductively Coupled Plasma Mass Spectrometer (ICP-MS): ELAN 9000 (Perkin Elmer Sciex Instrument, Concord, Ontario, Canada) (Jarvis et al. 1991).

Twenty-three soil samples (Fig. 1) were collected in March 2012 from the farming areas located along the Gulf of Aqaba coast. The samples were collected from the upper 10 cm section and placed in labeled polyethylene bags. To investigate the surrounding geologic materials as potential sources of metals in the soil, 24 rock samples were collected from granitic and marine origin sedimentary rocks. The soil and rock samples were placed in a dry and clean Teflon digestion beaker. Then, all specimens were digested by adding 6 ml HNO_3 , 2 ml HCl and 2 ml HF . The digested samples were then heated on a hot plate at 120–150 °C for approximately 40 min. In methods of decomposition losses of As as a result of volatilization in the form of AsCl_3 , AsF_3 , and AsH_3 must be prevented. In general, the sample decomposition of As should be carried out under oxidizing conditions (HNO_3 present). Arsenic is lost from fuming HClO_4 - HF solutions. Because the resulting ions after digestion remained unclear, the samples were filtered through Whatman filter paper No.42. Finally, the filtered digest was transferred to a 50 ml plastic volumetric flask and filled up to mark by deionized water. Dissolved metal contents were analyzed with an Inductively Coupled Plasma Mass Spectrometer (ICP-MS): ELAN 9000 (Perkin Elmer Sciex Instrument, Concord, Ontario, Canada) (Jarvis et al. 1991).

For quality control, replicates (approximately 20 % of the total number of samples) were analyzed under the same procedures as described earlier. A standard sediment reference material (BCSS-1) was digested and analyzed in a similar way to ensure quality control and accuracy. Analytical results of the selected samples reveal good agreement between the values of the referenced and those of the analyzed materials.

Assessment of arsenic pollution

Enrichment factor (EF) is used here to assess the level of heavy metals contamination and the metals' possible impacts on the soil quality in the Gulf of Aqaba area. Geochemical normalization of metals concentrations to

conservative elements, such as Al, Fe, or Si, has been employed to identify their anomalous zones. In the past decade, several authors have successfully used Fe to normalize metal contaminants (Çevik et al. 2009; Christophoridis et al. 2009; Meza-Figueroa et al. 2009; Bhuiyan et al. 2011; Ghrefat et al. 2011). In the present study, Fe is used as a conservative tracer to differentiate between natural and anthropogenic components.

The EF is defined by following formula (Ergin et al. 1991):

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

where $\left(\frac{M}{Fe}\right)_{\text{sample}}$ is the ratio of metal and Fe concentrations in the sample, and $\left(\frac{M}{Fe}\right)_{\text{background}}$ is the ratio of metal and Fe concentrations in the background.

In this study, the average concentrations of As in various lithological units exposed in the study area are taken as their background values, which in turn are used in calculating enrichment factor and geoaccumulation index.

EF values between 0.5 and 1.5 have been entirely linked to crustal materials (natural processes) as a source of metals in the soil, whereas the values >1.5 have been attributed to anthropogenic activities (Zhang and Liu 2002). According to Chen et al. (2007) classification, $EF < 1$ corresponds to no enrichment, $EF = 1-3$ to minor enrichment, $EF = 3-5$ to moderate enrichment, $EF = 5-10$ to moderately severe enrichment, $EF = 10-25$ to severe enrichment, $EF = 25-50$ to very severe enrichment and $EF > 50$ to extremely severe enrichment.

Index of geoaccumulation (I_{geo}) is defined by the following equation:

$$I_{\text{geo}} = \text{Log}_2 \left(\frac{C_n}{1.5B_n} \right)$$

where C_n is the metal content in the soil, B_n is the geochemical background value in shale (Turekian and Wedepohl 1961), and the factor 1.5 allows for possible changes in the background data due to lithological variations. The I_{geo} is classified into seven grades, among which the highest (grade 6) reflects a 100-fold enrichment above the background values (Müller 1981).

Statistical treatment

Statistical analyses were conducted by use of SPSS 20 (SPSS Inc., USA). Significance levels of $P < 0.05$ and 0.01 were used throughout the study. Correlations between the measured parameters were analyzed by Pearson product-moment correlation.

Discussion and results

Arsenic levels in groundwater samples

Table 1 summarizes the results for the analysis of As and other elements present in the groundwater samples. Concentrations of arsenic in fresh water depend on the source of arsenic, the amount available and the local geochemical environment. The greatest range and the highest concentrations of arsenic in the groundwater samples are due to the strong influence of water–rock interactions and the greater tendency in aquifers for the physical and geochemical conditions to be favorable for arsenic mobilization and accumulation. Arsenic concentrations in the study area ranged between <0.1 and 2.2 µg/L with a mean of 0.63 µg/L (Table 1). Concentrations of other elements were also quite low. To evaluate the safety of the groundwater samples for drinking purposes, concentrations of As and other elements in the present study were compared with the guidelines for drinking-water quality established by the WHO (2008) (Table 1). All the groundwater samples in the study area fell within the acceptable limits of the World Health Organization (WHO) guideline value of 10 µg/L for As in drinking water (WHO 2008).

Background concentrations of As in groundwater are less than 10 µg/l in most countries (Edmunds et al. 1989; Welch et al. 2000), and sometimes substantially lower. High concentrations of As are found in groundwater in a variety of environments. This includes both oxidizing (under conditions of high pH) and reducing aquifers and in areas affected by geothermal, mining and industrial activity.

Redox potential (Eh) and pH are the most important factors controlling As speciation. Under oxidizing conditions, $H_2AsO_4^{1-}$ is dominant at low pH (less than approximately pH 6.9), whereas at higher pH, $HAsO_4^{2-}$ becomes dominant. Under reducing conditions at pH less than approximately pH 9.2, the uncharged arsenite species $H_3AsO_4^0$ will predominate (Yan et al. 2000). In the present study, $HAsO_4^{2-}$ is the dominant As species in the groundwater samples. The pH values in the groundwater samples range between 7.02 and 7.82, with an average value of 7.44. The Eh values range between 355 and 394 mV with an average of 379 mV (Table 1). Previous studies demonstrated that arsenic in ground waters in some large areas in the Chaci-Pampean Plain of central Argentina, Lagunera (Mexico), and Antofagasta (Northern Chile) was found under oxidizing conditions and neutral-to-high pH (Smedley and Kinniburgh 2002). The increase in Eh values is due to enrichment of groundwater samples with dissolved oxygen during the percolation from the drainage area.

Arsenic levels in rock samples

Geochemical results obtained from the studied rock samples show a significant variation in mean metal contents (mg/kg) from one rock type to another (Table 2). The estimated average concentrations (mg/kg) of As and other elements in the collected rock samples are as follows: Fe (3075.2), Al (1823.5), V (24.7), B (15.4), Ba (11.4), As (6.9), Se (0.98), Sb (0.4), and Be (0.27) (Table 2). According to Bhumbra and Keefer (1994), the As content of rocks depends on the rock type, with sedimentary rocks containing much higher concentrations than igneous rocks.

Table 1 Descriptive statistics of the physico-chemical parameters in the groundwater samples collected along the Gulf of Aqaba

Element	Unit	Min.	Max.	Mean	SD	WHO (2008)
Al	µg/L	0.5	6.8	2.73	1.26	200
As		0.1	2.2	0.63	0.50	10
Au		0.2	8.6	1.04	1.68	–
B		4.4	22.8	10.85	4.79	500
Ba		3.3	100.8	28.34	28.05	700
Be		0.2	0.5	0.37	0.07	–
Fe		0.2	93	8.08	19.36	200
Sb		0.2	1.3	0.74	0.31	20
Se		0.1	3	1.25	0.92	10
Sn		0.2	0.5	0.37	0.10	–
Ti		0.1	1.4	1.04	0.40	–
V		0.4	12.6	6.27	2.84	–
pH	–	7.02	7.82	7.44	0.238	6.5–8.5
EC	µS/cm	830	20,500	4778	4465	–
Eh	mV	355	394	379	8.4	–

Table 2 Rock samples analysis for metal composition (mg/kg) ($n = 24$)

Sample no.	Rocks types	Description	Al	As	B	Ba	Be	Fe	Sb	Se	V	
1	Sedimentary rocks	Gypsum, shale and sand	504	6.4	54	7	0.2	1890	0.5	1.5	13	
2		Gypsum, shale	2485	8	38	3	0.4	6963	0.3	0.6	22	
3		Conglomerate and sandstone	1935	5	20	23	0.4	1789	0.3	0.9	18	
4		Conglomerate and sandstone	1223	9	25	79	0.5	3289	0.5	1.6	29	
5		Hemantic sandstone	129	12	18	4	0.05	263	0.4	1.6	24	
6		Anhydrite	165	6	5	1	0.03	324	0.02	0.4	8	
7		Gypsum—Marl	382	9	13	6	0.06	678	0.3	1	18	
8		Conglomerate	1103	6	10	2	0.2	932	0.4	0.9	25	
9		Coral reef	615	20	15	19	0.1	575	0.1	0.7	24	
10		Coral reef	979	10	15	18	0.02	819	0.06	1	31	
11		Coral reef	222	9	5	2	0.06	187	0.02	0.2	11	
12		Sandstone	1582	6	15	16	0.3	7256	0.1	0.9	32	
13		Sandstone with silica	1489	4	6	2	0.2	1581	0.06	0.5	16	
Descriptive statistics	Min		129	4	5	1	0.02	187	0.02	0.2	8	
	Max		2485	20	54	79	0.5	7256	0.5	1.6	32	
	Mean		985.62	8.49	18.38	14	0.19	2042	0.24	0.91	20.85	
	Std. deviation		738.96	4.12	13.98	20.99	0.16	2407.53	0.18	0.45	7.61	
14	Igneous Rocks	Granite	709	2	8	4	0.1	2309	0.02	1.3	17	
15		Granite	209	7	9	3	0.1	451	0.6	1	35	
16		Alkali feldspar granite (K-spar)	597	10	10	7	0.2	1777	0.04	2	58	
17		Granite	962	9	12	9	0.4	1260	0.03	1.3	31	
18		Granite	585	3	17	8	0.2	6707	0.03	1.3	23	
19		Rhyolite porphyritic dominated by quartz and plagioclase	597	2	9	4	0.1	765	0.01	0.6	11	
20		Granite dominated by quartz, K-feldspar, and hornblende	567	6	13	8	0.3	572	0.02	1	25	
Descriptive statistics		Min		209	2	8	3	0.1	451	0.01	0.6	11
		Max		962	10	17	9	0.4	6707	0.6	2	58
		Mean		603.71	5.57	11.14	6.14	0.2	1977.29	0.11	1.21	28.57
	Std. deviation		222.5	3.3	3.13	2.41	0.11	2191.22	0.217	0.429	15.27	
21	Metamorphic rocks	Metatuff	9243	7	10	2	0.5	8395	0.02	0.9	46	
22		Metavolcanic	9442	2	7	11	0.4	10,746	0.02	0.9	33	
23		Metasediments	4135	4	27	14	0.8	6767	0.03	0.6	24	
24		Metasediments	3906	3	8	21	0.8	7510	0.06	0.8	19	
Descriptive statistics		Min		3906	2	7	2	0.4	6767	0.02	0.6	19
	Max		9442	7	27	21	0.8	10,746	0.06	0.9	46	
	Mean		6681.5	4	13	12	0.625	8354.5	0.0325	0.8	30.5	
	Std. deviation		3075.15	2.16	9.42	7.87	0.21	1727.64	0.02	0.14	11.85	

Generally, the mean As concentrations in igneous rocks range from 1.5 to 3.0 mg/kg, whereas the mean As concentrations in sedimentary rocks range from 1.7 to 400 mg/kg. Arsenic levels in the sedimentary rocks of the study area range from 4 to 20 mg/kg with an average of 8.49 mg/kg. Some of the highest observed As concentrations are

found in hematitic sandstone. As levels in the coral reefs range from 9 to 20 mg/kg. Sands and sandstones tend to have the lowest concentrations, reflecting the low As concentrations of their dominant minerals, quartz and feldspars. Arsenic levels in the igneous rocks of the study area range between 2 to 10 mg/kg, with an average of

5.57 mg/kg. Boron levels in the sedimentary and igneous rocks of the study area vary from 5 to 54 mg/kg and 8 to 17 mg/kg, respectively.

Arsenic levels in soil samples

Table 3 summarizes the geochemical results of the collected soil samples. The results indicate that iron (Fe) has the highest average concentration (2259.7 mg/kg), whereas gold (Au) has the lowest concentration, with an average of 0.01 mg/kg. Arsenic is often found in combination with mineralized veins of ore containing copper, silver and gold (Smedley and Kinniburgh 2002). In many regions of the world, arsenic is used as a pathfinder element in gold exploration by tracking increasing concentrations of

arsenic in water. Arsenic concentrations in the soil samples varied from 2 to 19 mg/kg, with a mean of 7.35 mg/kg (Table 3). Boron concentrations in the soil samples varied from 3 to 19 mg/kg, with a mean of 9.14 mg/kg (Table 3). The highest concentrations of boron are found in sediments and sedimentary rock, particularly clay rich marine sediments. The studied elements in the study area (Table 3) were compared to various international standards to determine their compliance. All studied element values except As and B were below the Canadian Council of Ministers of the Environment’s soil quality thresholds (CA-SQG 2010).

The results demonstrated that the concentrations of As in the study area were generally below the values reported for average normal soils (Table 1). Worldwide total As levels in soils were found between 0.1 and 40 mg/kg (Bowen 1979), 0.1 and 55 mg/kg (Boyle and Jonasson 1984), 9 and 390 mg/kg (Patel et al. 2005), 0.88 and 4.96 mg/kg (Karim et al. 2008), 5.5 and 150 mg/kg (Sanchez et al. 2010), and 1.99 and 9.12 mg/kg (Solgi et al. 2012). The background concentration of As is less than 10 mg/kg in soils of the Salamanca province of Spain (Garcia-Sanchez et al. 2003). According to Adriano (2001), As values in uncontaminated agricultural soils range between 1 and 20 mg/kg. Boron is found naturally in soils at concentrations of 5–150 mg/kg.

The I_{geo} values (Table 4) reveal that the soil samples of the Gulf of Aqaba are uncontaminated to moderately contaminated with respect to As (Table 5), indicating a geogenic source for these metals. The I_{geo} seems to be a more objective tool for assessing contamination. The obtained results indicate that As received minor enrichment ($EF = 2.67$) (Table 5). Variation in EF values for As may be due to a difference in input magnitude of As in the studied soil. The values of enrichment factor in this particular case did not reveal the real As content in the soil. The EF values show that as the values of As vary the classification of contamination levels vary. The classification of contamination levels based on I_{geo} does not always vary as the contents of As vary. Consequently, the calculations of I_{geo} are more reliable than those of EF for assessing As pollution in the study area. Previous studies demonstrated that both I_{geo} and EF depend on the background data used, grain size, and bonding forms of metals (Turekian and Wedepohl 1961; Rubio et al. 2000, Yaqin et al. 2008; Ghrefat et al. 2011). Rubio et al. (2000) calculated I_{geo} for the sediments of Ria de Vigo, NW Spain,

Table 3 Statistical summary of the soil quality (mg/kg) in the study area ($n = 23$)

Element	Min.	Max.	Mean	SD
Al	164	3044	1111.65	824.11
As	2	19	7.35	5.46
Au	0.002	0.02	0.01	0.00
B	3	19	9.14	4.78
Ba	2.5	31	9.78	6.83
Be	0.05	1.4	0.22	0.28
Fe	486	5511	2259.70	1434.65
Sb	0.008	0.3	0.08	0.06
Se	0.1	0.7	0.30	0.16
Sn	0.04	2	0.30	0.39
Ti	10	119	46.43	27.09
V	12	72	31.00	18.16

Table 4 Geoaccumulation index (I_{geo}) (Müller 1981) for contamination levels in sediments

I_{geo} class	I_{geo} value	Contamination level
0	$I_{geo} \leq 0$	UC
1	$0 < I_{geo} < 1$	UC/MC
2	$1 < I_{geo} < 2$	MC
3	$2 < I_{geo} < 3$	MC/SC
4	$3 < I_{geo} < 4$	SC
5	$4 < I_{geo} < 5$	SC/EC
6	$5 < I_{geo}$	EC

UC Uncontaminated, MC moderately contaminated, SC strongly contaminated, EC extremely contaminated

Table 5 Descriptive statistics of EF and I_{geo} calculations for As in the soil samples

Variable	Min.	Max.	Sum	Mean	SD	Variance	Skewness	Kurtosis
EF	0.22	17.45	61.61	2.6787	3.76477	14.173	3.016	10.911
I_{geo}	0.00	0.88	3.21	0.1396	0.27220	0.074	1.823	2.029

using three different background values The results show that significant differences are observed between backgrounds used for Cr, Pb, and Cu.

Arsenic values in the rock samples range from 2 and 20 mg/kg with an average of 6.9 mg/kg (Table 2). In the studied soil samples, the concentrations of Al, Ba, Be, Fe, Sb, and Se are higher than are those obtained from the rock samples (Table 3). Average arsenic concentrations in open seawater usually show little variation and are typically approximately 1.5 µg/l. Boron is a common element in marine water, with a typical concentration of 4.5 mg/l (Butterwick et al. 1989). High recorded values of As and B in the soil samples are mainly due to the weathering of rocks, seawater inputs, and anthropogenic sources including agricultural activities (Dotsika et al. 2011). Al-Taani et al. (2014) found that boron values in seawater collected from the Saudi Gulf of Aqaba coast range from 0.198 to 2.9 mg/l with an average of 1.916 mg/l. Arsenic values

range between 0.46 and 1.55 µg/l with an average of 0.82 µg/l.

Statistical analysis

Correlation analysis (CA)

Tables 6 and 7 summarize Pearson’s correlation coefficient matrix between As and other elements in the collected groundwater, soil, and rock samples. The correlation matrix analysis provides a good tool to better understand the complex dynamics of pollutants in the environment. A very significant positive correlation is found between As and Au ($r = 0.66$), As and B ($r = 0.60$), As and V ($r = 0.96$) in the soil samples at 0.05 level. Additionally, Arsenic in the rock samples demonstrate significant correlation with V and Ba ($r = 0.44$ and 0.72 , respectively). In the groundwater samples, As only shows significant

Table 6 Pearson correlation coefficient between metal concentrations in the rock samples

	Al	As	B	Ba	Be	Fe	Sb	Se	V
Al	1								
As	-0.254	1							
B	-0.143	0.069	1						
Ba	0.134	0.372*	-0.163	1					
Be	0.555**	-0.164	0.075	0.361*	1				
Fe	0.807**	-0.057	-0.085	0.365*	0.584**	1			
Sb	-0.028	-0.177	-0.173	0.359*	0.052	-0.077	1		
Se	-0.189	0.093	0.371*	-0.249	-0.093	-0.244	-0.357*	1	
V	0.3	0.440*	-0.152	0.286	0.26	0.314	-0.102	0.387*	1

* $p < 0.05$

** $p < 0.01$

Table 7 Pearson correlation coefficient between metal concentrations in the soil samples

	Al	As	Au	B	Ba	Be	Fe	Sb	Se	Sn	Ti	V
Al	1.00											
As	-0.15	1.00										
Au	-0.26	0.663**	1.00									
B	-0.14	0.604**	0.656**	1.00								
Ba	0.744**	0.05	-0.15	-0.26	1.00							
Be	0.13	-0.03	-0.18	-0.15	0.28	1.00						
Fe	0.797**	-0.13	-0.33	-0.27	0.692**	0.566**	1.00					
Sb	0.634**	0.18	0.12	0.15	0.730**	0.41	0.615**	1.00				
Se	0.457*	-0.01	-0.13	0.01	0.34	0.703**	0.691**	0.534**	1.00			
Sn	0.33	-0.16	-0.10	0.21	0.15	0.12	0.29	0.23	0.19	1.00		
Ti	0.780**	-0.09	-0.13	-0.22	0.759**	0.467*	0.901**	0.713**	0.530**	0.35	1.00	
V	-0.12	0.965**	0.594**	0.569**	0.04	0.07	-0.04	0.18	0.09	-0.10	-0.03	1.00

* $p < 0.05$

** $p < 0.01$

correlation with Sn ($r = 0.55$). A significant negative correlation between Ba and T ($r = -0.87$) and Be and V ($r = -0.49$) was observed. The high positive correlation of As with some of the studied metals indicates their common sources, may be rock leaching and weathering in the study area.

Conclusions

The current study presents useful tools and geochemical indices for the evaluation of heavy metal pollution in the soil. Furthermore, this study provides a powerful tool for processing, analysing and conveying raw environmental information for decision-making processes and management involving natural resources. The present study reveals a considerable variation in the concentrations of As and other metals in the soil and groundwater samples. This may be due to a change both in the intensity of agricultural activities and in the degree of weathering of the lithological units. All the groundwater samples fall within the permissible limits of As for drinking water set by the World Health Organization (WHO) and were found to be safe with respect to As and other elements. Arsenic in the collected groundwater samples occurs in the fully oxidized state of plus 5 (As^{+5}), in the form of HAsO_4^{2-} under existing oxidizing and pH conditions. The studied rock samples in the study area show a significant variation in mean metal content from one rock type to another. Sedimentary rocks in the study area recorded higher concentrations of As and other metals when compared with the igneous rocks. The average concentrations of most of the studied elements in the soil of the study area are found to be lower than the globally determined averages for the same metals in normal soils. Based on the I_{geo} and EF values, the soil samples have been found to be unaffected in terms of arsenic contamination. The calculations of I_{geo} are found to be more reliable than of those of EF for Arsenic contamination levels assessment. The elevated values of As and B in the studied soil samples are mainly due to agricultural activities and seawater inputs. The correlation matrix analysis provides an important tool for better understanding the complex dynamics of pollutants. The results of the Pearson's correlation matrix analysis demonstrate that metals in the study area exhibit different degrees of correlation due to their different sources.

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