Research Article

Evaluation of Groundwater for Arsenic Contamination Using Hydrogeochemical Properties and Multivariate Statistical Methods in Saudi Arabia

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The aim of this research is to evaluate arsenic distribution and associated hydrogeochemical parameters in 27 randomly selected boreholes representing aquifers in the Al-Kharj geothermal fields of Saudi Arabia. Arsenic was detected at all sites, with 92.5% of boreholes yielding concentrations above the WHO permissible limit of $10\,\mu g/L$. The maximum concentration recorded was $122\,\mu g/L$ (SD = $29\,\mu g/L$ skewness = 1.87). The groundwater types were mainly Ca^{+2}-Mg^{+2}-SO_4^{-2}-Cl^- and Na^+-Cl^--SO_4^{-2}, accounting for 67% of the total composition. Principal component analysis (PCA) showed that the main source of arsenic release was geothermal in nature and was linked to processes similar to those involved in the release of boron. The PCA yielded five components, which accounted for 44.1%, 17.0%, 10.1%, 08.4%, and 06.5% of the total variance. The first component had positive loadings for arsenic and boron along with other hydrogeochemical parameters, indicating the primary sources of As mobilization are derived from regional geothermal systems and weathering of minerals. The remaining principal components indicated reductive dissolution of iron oxyhydroxides as a possible mechanism. Spatial evaluation of the PCA results indicated that this secondary mechanism of arsenic mobilization may be active and correlates positively with total organic carbon. The aquifers were found to be contaminated to a high degree with organic carbon ranging from 0.57 mg/L to 21.42 mg/L and showed high concentrations of NO_3^- ranging from 8.05 mg/L to 248.2 mg/L.

1. Introduction

Arsenic is a toxic and carcinogenic metalloid which is geogenic in origin and has been shown to be detrimental to human health when present in the environment [1, 2]. The major source of human exposure to arsenic is drinking water. In order to check its adverse effects the World Health Organization (WHO), the US Environmental Protection Agency (USEPA), and the European Commission have proposed guideline for arsenic in water ($10\,\mu g/L$). Arsenic has been shown to occur in shallow aquifers above the limit in groundwaters across the world [3]. Arsenic had been shown also to occur in groundwater of arid and semiarid environments [4, 5]. There have been reports of occurrence of arsenic in Saudi Arabian aquifers, and the arsenic contamination of groundwater could potentially have wider effects due to the

use of groundwater as a main source of water in Saudi Arabia [6, 7].

Arsenic mobilization in groundwater is linked to geologic setting and sedimentary components, which control the geochemistry and release of As into groundwater from bedrocks. The geochemistry of groundwater is dominated by redox processes occurring at the sediment-water interface. Adsorption capacity of the mineral surfaces also depends on geochemical parameters, such as pH, electrical conductivity (EC), ionic composition, and mineral type. Thus hydrogeochemical characteristics, such as the oxidation state of the mineral phases, and the associated cofactors affecting arsenic-containing solid phases, are responsible for arsenic mobilization. Aquifers with high arsenic content are characterized by high concentrations of bicarbonate, high pH and dissolved iron under reducing conditions and by sulfate, low

pH, and iron precipitate under oxic conditions [8, 9]. Arsenic exists in two interconvertible oxidation states, As(III) and As(V). As(III), or arsenite, exists as an uncharged species (H_3AsO_3), whereas the dominant As(V) or arsinate exists as anions ($H_2AsO_4^{-}$ and $HAsO_2^{4-}$). Arsenic as a redox sensitive contaminant is proposed to obtain mobility in aquifers mainly by dissolution of Fe oxides of As into the aqueous phases [10, 11]. This process is especially shown to be biologically mediated in the presence of organic matter [12]. There has also been enormous amount of research done in relation to elevated concentrations of As in geothermal fields and hot springs. High levels of As, B, Fe, Mn, and Sb occur due to mixing of cold waters with geothermal fluids and are often associated with a high total dissolved solids (TDS) [13]. The Saudi Arabian aquifers are formations existing in the Arabian shield and the Arabian shelf of the quaternary and cenozoic age. These are dozens of hot springs scattered across the country and are sometimes the subject of exploration for renewal energy [14]. A study carried by Bazuhair et al. in 1990 indicates Al-Kharj to have had hot springs, since then the hot springs have dried due to decrease in water table but the geothermal gradient exists in the deep aquifer environment [15].

Studies of arsenic hydrogeochemistry and mobilization often involve evaluation of numerous factors, and these factors can be analyzed with multivariate statistics to elucidate underlying processes. Processes like carbonate dissolution, silicate weathering, and ion exchange were found to control major-ion chemistry by using the geochemical modeling and principal component analysis [16]. Hierarchical cluster analysis (HCA) and principal components analysis (PCA) were used to elucidate aquifer geochemistry and understand evolution of hydrogeochemical characteristics of groundwater in 153 sites over a 1500 sq·km^2 area [17]. Geothermal waters from geothermal wells and hot springs were classified into two factors, one indicating the reservoir temperature distribution and the other indicating hydrogeochemical processes resulting from the CO_2 pressure decrease in geothermal water during its ascent towards the ground surface [18]. Estimation of total arsenic and inorganic speciation for surface and groundwater samples was performed by using principal component analysis, cluster analysis, metal-to-metal correlations, and linear regression analyses [19].

The aim of this work is to (i) report the detection of As above the WHO permissible limit in Al-Kharj geothermal fields, which has been done for the first time from this region and (ii) quantitatively evaluate the Al-Kharj area for arsenic contamination $[As]_{tot}$, moreover, information on hydrogeochemical parameters [pH, EC, TDS, major anions (HCO_3^{-}, NO_3^{-}, Cl^{-} and SO_4^{-2}) and major cations (Ca^{+2}, Mg^{+2}, Na^{+} and K^{+})] has been obtained to characterize the quality of water as it relates to the As data. Furthermore, relevant data on trace elements (Fe, Mn, Li, and Sb) to delineate arsenic geochemistry in the study area is also collected. The large dataset is subjected to multivariate statistics, using Principle Component Analysis (PCA) and Cluster Analysis (CA) techniques to determine similarities and dissimilarities in hydrogeochemical properties, and to make predictions about the As mobilization processes in aquifers of Al-Kharj region.

2. Materials and Methods

2.1. Geology and Hydrogeology. The studied region is Al-Kharj agricultural area, located southeast of Riyadh in Saudi Arabia (23°59′N 47°09′E-24°22′N 47°06′′′E) (Figure 1). Al-Kharj is one of the five major agricultural regions in the country, surrounded by Wadi Dawasir, Hofuf, Gassim and Taif in the southwest, northeast, northwest, and west, respectively, of the region. The climate in this area is typically arid, with an annual precipitation of 132 mm. Al-Kharj is considered to be a lowland with alluvium deposition. The soil type is entisol and aridisol with saline and calcareous profiles [20]. The aquifers in Al-kharj are contained within the Eocene Dammam Formation and Miocene-Pleistocene sedimentary rocks present within the stable shelf tectonic unit between the Arabian shelf and western Precambrian shield [21, 22]. Major recharge of the aquifer systems in this region has been estimated to have occurred during pluvial periods, some 25,000 to 30,000 years ago, based on isotopic methods (stable carbon, oxygen, and hydrogen) [23, 24]. The recharge of these aquifers has been estimated to occur at a rate of 15% of the total annual rainfall that is, 100 mm approximately [25, 26].

2.2. Sampling and Analytical Methods. The groundwater sampling was collected from 27 boreholes in and around the centrally habitated Al-Kharj agricultural area (Figure 1). The boreholes were purged to about three borehole volumes before the sampling was done; the pH and EC were measured on spot to obtain instantaneous and stabilized measurements. The samples were collected in polypropylene containers which were previously cleaned and prepared with 5 M HNO_3. The samples were analyzed for major ions (Na^{+}, K^{+}, Ca^{+2}, Mg^{+2}, HCO_3^{-}, Cl^{-}, and SO_4^{-2}) and some minor ions (NO_2^{-} NO_3^{-}) using the standard protocols suggested in American Public Health Association, (APHA, AWWA, WAF) [27]. Groundwater samples were filtered by 0.45 μm Millipore filter paper and acidified with 2N HNO_3 (Ultra pureMerck) for cation analysis and trace metal measurements. The anions NO_2^{-} NO_3^{-}, Cl^{-}, and SO_4^{-2} were analyzed using the Ion Chromatograph-Conductivity Detection (Shimadzu, LC-20AD-SP, Non-Suppressor) with Shim-pack IC-A3 (150 mmL. 4.6 mm I.D.) column and 8.0 mM p-Hydroxybenzoic Acid: 3.2 mM Bis-Tris as mobile phase at 1.5 mL/min flow rate and 40°C using Electric Conductivity Detector (ECD). The trace element data was obtained by acidifying and subjecting to analysis using the ICP-OES (Perkin Elmer, Model 4300 DV). Sodium and Potassium were measured using flame photometry and calcium and magnesium were measured using the ICP-OES. TOC is measured by high temperature catalytic oxidation method using Shimadzu TOC-VCPN analyzer [28]. As the TOC in groundwater is mainly composed of the inorganic carbon in comparison to a relatively very minimal amount of organic carbon, nonpurgeable organic carbon (NPOC) method is used to quantitate the organic carbon. In this method first the total
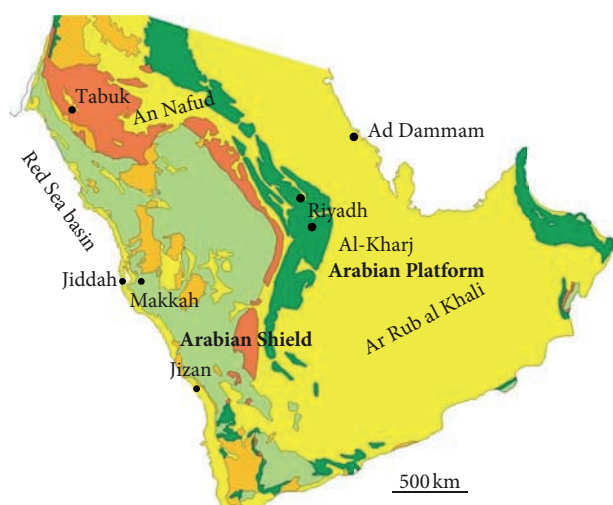
(a)

(b)

FIGURE 1: Geography of studied region of Al-Kharj Governorate in Riyadh Province East of KSA (a). The geographical layout of sedimentary rock formation in Saudi Arabia (adapted from: Saudi Geological Survey, 2008). (b) The GPS location indicating the sampling location in the Al-Kharj region in central Saudi Arabia.

inorganic carbon (TIC) is purged before any organic carbon measurement is performed; the remaining organic matter is then oxidised to CO_2 and quantified as nonpurgeable organic carbon (NPOC). The concentration of HCO_3^- was determined by acid titration.

2.3. Statistical Analysis and Data Treatment. The correlation between the arsenic concentrations and physiochemical properties of groundwater was obtained in the form of Pearson correlation coefficients from the raw data. Principal component analysis (PCA) was used to reduce large number of variables to representative factors called "Principal Components". The aim was to delineate underling processes defined by parameters/variables like the physiochemical properties of groundwater, organic content, and trace element data. The components accounting for the maximum variance in the PCA output were chosen as significantly relating to the arsenic hydrogeochemistry. Proc factor procedure in the Statistical Analysis Software (SAS) was used to compute the eigenvalues and the components with eigenvalues greater than one were considered. Varimax rotation of component matrix was performed to maximize the variance between the components and simultaneously reduce the number of variables having high loading/score in each component to facilitate easy interpretation of the components. Hierarchical cluster analysis (HCA) was used as classifying tool aiming to club different sampling locations in the Al-Kharj region into few clusters with common underlying structures and to possibly explain the components obtained from PCA as detailed [29]. The clustering was done on the basis of Wards-algorithmic and shown in the form of dendrograms (Squared Euclidian distances). The multivariate analysis dataset essentially comprised of both the physiochemical properties with high numeric range and trace metal data with

low numeric range, therefore before performing the PCA or HCA, data transformation/standardization was done to avoid the uneven contribution of few variables with high numeric values on the overall variance in the analysis. For effective scaling, the following transformation was applied:

$$Z_{ij} = \frac{X_{ij} - \mu_j}{\sigma_j}, \qquad (1)$$

where Z_{ij} is the transformed variable, X_{ij} is the actual variable, μ_j is the mean for a specific variable, and σ_j in the dataset is the standard deviation, SD. This scaling method was selected as it represents the best data transformations methods for data with least number of outliers (extreme Maxima and Minima). Quality control was assured by fitting the data to normal distribution plots (not shown in paper). The variables were fairly linear, and any outliers were detected and dealt with before executing the multivariate methods. Data transformations, linear regression, and other multivariate methods were performed either by using the MS excel or the SAS statistical software (SAS Institute, Inc., 1998).

3. Results and Discussion

3.1. Hydrogeochemical Properties and Geothermal Tracers. The geochemical parameters for groundwater in Al-Kharj are given in Table 1. Thirteen parameters (pH, electrical conductivity (EC), total dissolved solids (TDS), Na^+, K^+, Ca^+, Mg^+, HCO_3^-, Cl^-, SO_4^{2-}, NO_2^-, NO_3^-, TOC), and trace elements data including $[As]_{tot}$, $[Fe]_{tot}$, Mn. Sb, Li, B were measured in 27 monitoring boreholes (Tables 1, 2). The pH values ranged between 6.65 and 8.28, which indicate a slightly acidic to slightly basic groundwater condition. Compared with the range of 6.5 to 8.5 prescribed by WHO for drinking

TABLE 1: Hydrogeochemical parameters of Al-Kharj groundwater forming the characteristic of aquifers spread in an area of 50 sq.Km.

S/N	pH	EC mS/cm	TDS μg/L	Na$^+$ (mg/L)	K$^+$ (mg/L)	Ca$^+$ (mg/L)	Mg$^+$ (mg/L)	HCO$_3^-$ (mg/L)	Cl$^-$ (mg/L)	NO$_2^-$ (mg/L)	NO$_3^-$ (mg/L)	SO$_4^{2-}$ (mg/L)	TOC (mg/L)
AGW01	7.11	1.650	1056	214.8	1.08	136.5	56.90	403.5	94.6	1.35	24.15	525.8	14.47
AGW02	7.38	1.664	1064.96	286.4	9.24	150.8	51.78	333.6	119.85	4.21	39.5	676.95	7.69
AGW03	7.27	2.309	1477.76	273.6	12.32	207.2	85.81	338.5	188.75	2.76	24.5	870.25	9.50
AGW04	7.45	2.251	1440.64	291.5	13.43	194.7	84.50	348.6	146.65	1.35	8.05	1327.5	14.04
AGW05	7.07	5.113	3272.32	461.6	24.37	477.2	156.5	427.3	454.1	4.89	111.4	2726.5	13.00
AGW06	7.24	3.451	2208.64	349.1	12.94	246.2	94.62	403.1	297.55	3.78	57.2	1765.15	11.14
AGW07	7.51	2.663	1704.32	314.5	11.79	203.9	82.43	351.5	189.65	3.87	46.9	1190.2	9.24
AGW08	7.73	4.184	2677.76	361.8	21.89	304.1	116.1	327.1	243.3	4.88	26.5	3053.55	8.75
AGW09	6.65	6.030	3859.2	452.6	40.99	334.7	171.0	742	481.2	5.79	53.45	3535.4	21.42
AGW10	7.52	5.905	3779.2	466.7	48.25	339.9	176.3	429.2	458.35	13.19	99.6	3540.15	13.78
AGW11	7.31	7.236	4631.04	520.4	31.68	459.7	163.6	400.6	1815.27	1.17	116.64	3128.76	11.66
AGW12	7.70	5.308	3397.12	259.5	20.39	461.6	141.9	244.7	1229.53	1.71	221.52	1767.37	9.02
AGW13	7.71	1.393	891.52	187.9	10.20	102.0	40.76	326.7	291.68	8.74	65.31	492.17	7.31
AGW14	7.84	2.996	1917.44	323.5	21.80	330.8	58.31	231.1	360	10.05	137.70	1493.37	5.54
AGW15	7.30	2.912	1863.68	276.2	23.65	360.1	85.84	449.4	265.54	4.85	81.42	1657.25	11.96
AGW16	7.29	1.671	1069.44	214.8	12.11	128.4	52.01	339.3	204.07	2.33	27.40	745.17	7.89
AGW17	7.03	3.016	1930.24	265.9	13.97	211.8	82.25	449.4	261.47	1.97	22.06	1399.13	9.64
AGW18	7.56	3.277	2097.28	290.2	15.55	304.6	76.77	297.9	364.92	5.64	63.53	1853.74	7.89
AGW19	7.39	3.226	2064.64	319.6	26.16	249.8	65.05	262.7	299.77	6.48	38.07	1418.04	6.82
AGW20	8.24	290.2	185728	104.8	1.95	16.31	3.75	24.8	59.28	0.63	11.54	101.93	0.574
AGW21	7.35	4.187	2679.68	341.4	24.90	445.6	85.45	171.9	361.3	0.30	179.85	1955	4.07
AGW22	7.67	4.644	2972.16	359.3	16.91	359.7	87.40	301.5	464.7	5.38	248.2	1834.55	6.76
AGW23	7.17	4.094	2620.16	313.2	21.52	455.2	93.74	328.9	377.3	2.79	136.2	1965.95	8.27
AGW24	7.40	2.124	1359.36	182.8	10.35	217.6	58.52	338.5	125.9	0.32	21.9	1213.3	7.21
AGW25	8.28	2.717	1738.88	290.2	23.86	363.7	86.17	578.4	190.85	3.45	98.55	1747.5	15.55
AGW26	7.51	2.090	1337.6	213.5	12.12	192.3	53.92	338.5	124.7	0.71	40.75	1139.2	8.08
AGW27	7.93	50.73	32467.2	1589.5	36.33	249.3	210.2	226.9	275.32	1.09	26.22	158.74	7.52

water, our values were within the desirable 6.5 to 9.5 range [30]. The maximum EC was recorded as 290.2 μS/cm, and the minimum was 1.39 μS/cm. The maximum TDS value was 2,06,042 mg/L, and the minimum was 989.11 mg/L. According to the TDS classification, 33.3% of the sampling sites were fresh water (TDS < 2000), 59.2% of the sampling sites were brackish water (2000 < TDS < 10000), and 7.4% were saline (TDS > 10000) [31]. The TDS values were markedly higher compared with reported values from the Arabian shield aquifers situated in Wadi Marwani, central western Saudi Arabian indication of geothermal activity [32]. The cations in considerably high concentrations were Na$^+$ and Ca$^+$, which ranged from 104.8 mg/L to 1589.5 mg/L, and 136.5 mg/L to 249.3 mg/L, respectively. K$^+$ and Mg$^+$ were in the range of 1.08 mg/L to 36.33 mg/L, and 56.9 mg/L to 210.2 mg/L, respectively. The anions in considerably high concentrations were SO$_4^-$ and HCO$_3^-$, which ranged from 24.8 mg/L to 742 mg/L, and 101.93 mg/L to 3535.4 mg/L, respectively. The other cations in the study (Cl$^-$, NO$_2^-$, and NO$_3^-$) were in the range of 59.28–1815.27, 0.3–13.19, 8.05–221.52 mg/L, respectively. The nitrate and nitrite concentrations appeared to be typical, compared with studies reported from other regions in Saudi Arabia [33]. The tendency for NO$_2^-$ and NO$_3^-$ to increase, due to agricultural activity has been demonstrated in Saudi Arabia and other countries [34, 35]. A brief evaluation of the dataset suggests that cations Ca$^+$ and Na$^+$ were quantitatively more abundant than cations K$^+$ and Mg$^+$. Likewise, anions Cl$^-$ and SO$_4^{2-}$ were quantitatively more abundant than anions HCO$_3^-$ and NO$_3^-$. Nitrate and Nitrite were detected at all the sites, but nitrite is quantitatively less than the nitrate, high levels of nitrate quantities reflect intensive use of fertilizers in the studied region. A careful study of the major ion chemistry of the collected groundwater can reveal the flow path of the aquifer because high Ca$^+$: Mg$^+$ ratios, low SO$_4^{2-}$, and high HCO$_3^-$ occur at the recharge zones. Conversely, the opposite conditions generally prevail in discharge zones. In addition, the flow pattern of the aquifer system in the Dammam Formation is believed to be in the upward and northerly direction [21, 36].

Arsenic was detected at all the sites, with 92.5% of the boreholes showing concentrations above the WHO permissible limit of 10 μg/L, with a maximum of 122 μg/L [37]. Manganese and iron were linked to arsenic release from the bedrock interface in the aquifer system. Manganese was detected in the range of 6 μg/L to 14 μg/L, and iron was detected within the range of 129 μg/L to 236 μg/L.

TABLE 2: Trace element data for Al-Kharj groundwater forming the characteristic of aquifers spread in an area of 50 sq. Km.

S/N	Li (mg/L)	Sb (mg/L)	Mn (μg/L)	$[As]_{tot}$ (μg/L)	Fe (μg/L)	B (mg/L)
AGW01	0.049	0.012	6	31	129	0.0252
AGW02	0.062	0.272	1	2	139	0.445
AGW03	0.071	0.317	2	6	89	0.349
AGW04	0.074	0.556	3	17	249	0.388
AGW05	0.138	1.053	3	14	93	1.833
AGW06	0.081	1.051	1	25	49	0.548
AGW07	0.074	0.861	3	23	65	0.752
AGW08	0.125	0.539	13	20	173	1.013
AGW09	0.137	0.372	1	31	88	2.272
AGW10	0.203	ND	11	55	76	2.056
AGW11	0.151	0.661	4	88	75	1.350
AGW12	0.103	0.413	7	122	203	0.284
AGW13	0.052	ND	1	73	56	0.257
AGW14	0.123	ND	3	38	85	0.702
AGW15	0.123	0.776	6	30	560	0.601
AGW16	0.062	0.440	1	27	67	0.293
AGW17	0.093	0.599	7	25	145	0.567
AGW18	0.091	0.595	2	15	60	0.446
AGW19	0.121	1.085	14	17	236	0.515
AGW20	0.009	0.406	2	16	68	0.459
AGW21	0.107	0.115	1	16	95	0.537
AGW22	0.085	0.155	1	17	95	0.537
AGW23	0.130	1.158	1	20	59	0.663
AGW24	0.140	0.089	ND	18	42	0.290
AGW25	0.114	0.107	4	22	69	0.532
AGW26	0.063	0.003	1	26	256	0.327
AGW27	0.210	0.003	5	75	151	4.254

*ND: below the detection level.

This indicated that iron was quantitatively more abundant than manganese in the aquifer strata, a characteristic of the minerals present, and part of the mineralization process. Boron was detected at all the sampling sites, with a range of 25–4254 μg/L. Lithium concentrations were detected between 9–210 μg/L, while antimony was detected in the range of 0–1158 μg/L. The detection of high concentrations of boron, antimony, lithium, and a correlation coefficient of $R^2 = 0.6$ between boron and arsenic indicates the presence of geothermal activity in the region [13]. Also the correlation of lithium and boron is 0.56 indicating the presence of geothermal activity in the area as boron and lithium are considered as geothermal tracers [13]. Piper diagrams traditionally have been used to understand groundwater chemistry processes, and to predict the nature and origin of water types. Figure 2 shows piper diagrams with respect to major sedimentary facies. Groundwater mainly was composed of Ca^{+2}-Mg^{+2}-SO_4^{-2}-Cl^- and Na^+-Cl^--SO_4^{-2} types, accounting for 67% of the total. Two major types of hydrochemical facies accounting for 67% and remaining to 33% of the hydrochemical facies may reflect a distinct fracture pattern in the lithology of

the region [15] and could determine the arsenic release mechanism.

3.2. Identification of Main Processes Causing the Release of Arsenic. The principal component analysis of standardized parameters resulted in five components with eigenvalues of 7.0518, 2.7257, 1.6086, 1.3456, 1.0368, accounting for 44.1%, 17.0%, 10.1%, 08.4%, and 06.5% of the total variance, respectively (Tables 3, 4). Although PCA can provide as many components as the number of variables, only those components with eigenvalues greater than one were considered. The first component had positive loading for all parameters, except for pH and Fe. The second component had a positive loading for all parameters, except pH, TDS, Ca^+ Cl^-, NO_3^- Mn, and As. The third component had a positive loading for all parameters, except TDS, Na^+, K^+, Ca^+, Mg^+, HCO_3^-, Cl^-, NO_3^-, TOC, and As. The fourth component had positive loading for all parameters, except TDS, Mg^+, HCO_3^-, Cl^-, NO_3^-, TOC Mn, As and Fe, and the fifth component had positive loading for all parameters, except TDS, Na^+, K^+, Ca^+, NO_3^-, SO_4^-, Mn, Fe, and B. The first component (PC1) has a positive loading for arsenic and boron with negative loadings for Fe. This indicated that this component accounted for the maximum variance of the PCA and was representative of arsenic and boron release due to geothermal systems and mineral weathering [38–40]. This can be confirmed by the observation that boron correlated with Na^+ and SO_4^{-2}, with values of 0.82 and 0.71, respectively. Also arsenic correlation with iron is poor ($R^2 = 0.0018$) and Fe has a negative factor loading in the PC1. Moreover, arsenic has been shown to be relatively soluble in hot and warm hydrothermal fluids [41]. The subsequent principal components supported this interpretation.

The second component (PC2) indicates the reductive dissolution of iron oxides as a possible mechanism. This component had a maximum loading for TOC and HCO_3^- and a positive high loading for Fe. Spatial evaluation indicated that a secondary mechanism of mobilization could be active and has a positive correlation with TOC. This mechanism relates to biologically mediated arsenic release due to the reductive dissolution of iron containing oxide from the mineral phase in the presence of organic matter [12]. Sites 6, 8, 15, 16, 17, 18, and 19, which constituted 25% of the total composition, had an R^2 of 0.53. The presence of freely dissolved iron in groundwater obtained from agricultural areas of the Al-Kharj region has been shown in other studies [42]. The two prominent types of mechanisms occurring in the subsurface sediments can be understood further by cluster analysis. Cluster analysis of the sampling sites with regard to As and B resulted in two distinct structural groupings, sites 2, 18, 3, 25, 16, 23, 4, 12, and 13, and another group of 6, 20, 21, 24, 19, 17, 15, 7, 14, and 22 (Figure 3). The presence of two distinct clusters in the pattern for As and B indicates the underlying communality in relation to hydrogeochemical properties. The deviation from a single main cluster could be due to the K^+ and PO_4^{-3} present in the aquifer, as Al-Kharj is an agricultural region and has a considerable amount of fertilizer input and from leaching of fertilizers and pesticides

TABLE 3: Pearson correlation matrix for the hydrochemical properties indicating the extent of effect of parameters.

	pH	EC (μS/cm)	Na$^+$	K$^+$	Ca$^+$	Mg$^+$	HCO$_3^-$	Cl$^-$	HNO$_3^-$	SO$_4^-$
EC (μS/cm)	0.469									
Na$^+$	0.113	−0.026								
K$^+$	−0.116	−0.242	0.561							
Ca$^+$	−0.174	−0.411	0.207	0.630						
Mg$^+$	−0.210	−0.272	0.725	0.826	0.617					
HCO$_3^-$	−0.519	−0.520	−0.013	0.374	0.241	0.381				
Cl$^-$	−0.101	−0.152	0.153	0.422	0.614	0.526	0.076			
HNO$_3^-$	0.105	−0.208	−0.014	0.297	0.735	0.244	−0.098	0.531		
SO$_4^-$	−0.347	−0.344	0.014	0.706	0.720	0.607	0.521	0.502	0.370	
As (ug/L)	0.183	−0.055	0.343	0.349	0.270	0.485	−0.049	0.709	0.347	0.108
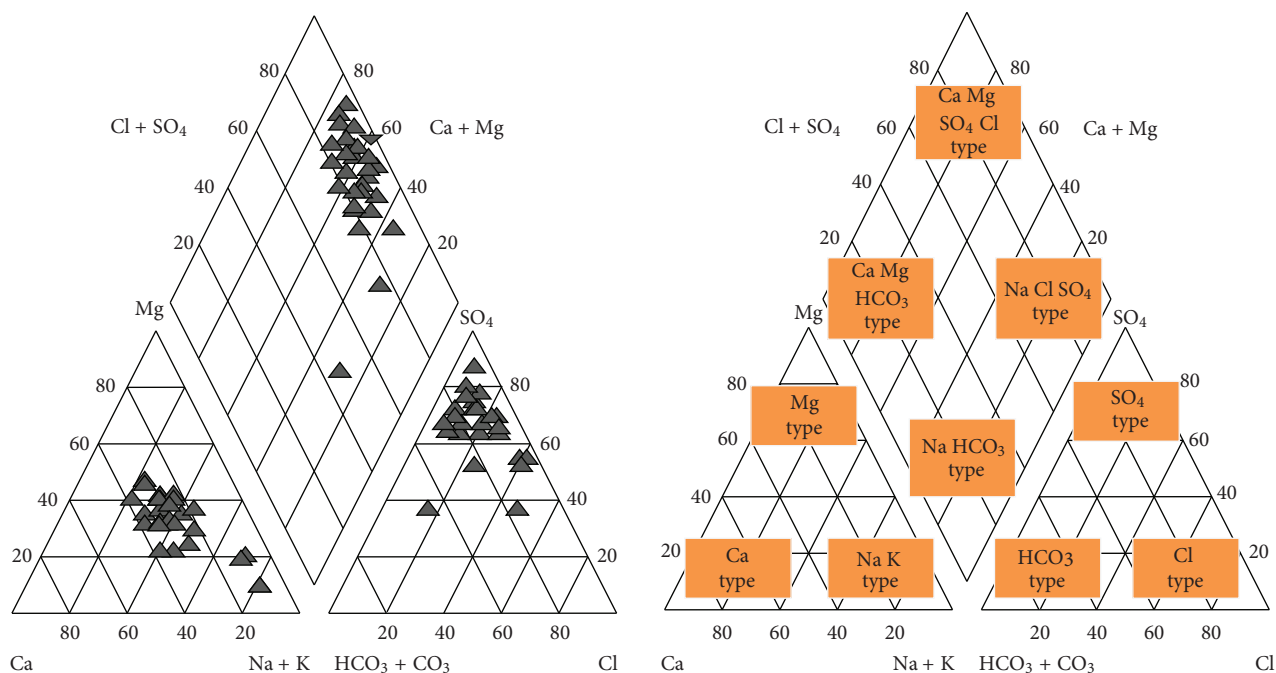
FIGURE 2: Piper diagram displaying the major ions present in the groundwater, indication of Ca^{+2}-Mg^{+2}-SO$_4^{-2}$-Cl$^-$ and Na$^+$-Cl$^-$-SO$_4^{-2}$ type of water in the aquifer environment.

added from anthropogenic sources, this could impact the subsurface geochemistry. This dendrogram can represent the PC1 obtained from the principal component analysis. The second dendrogram in Figure 3 refers to the clustering of sites with respect to As, Fe, Mn, TOC, NO$_3^-$, HCO$_3^-$. The dendrogram provides numerous unclear clusters and the level of similarity lying in the subclusters is less (Similarity expressed as % on y-axis of the dendrograms), indicating the interaction of various factors involved along with the process of mobilization of arsenic through reductive dissolution of ferrous oxyhydroxide. This dendrogram can represent the PC2, PC3, PC4, and PC5 components. While PC1 and PC2 are being recognized as the main components and this fits well with the water type classification which is mainly two types Ca^{+2}-Mg^{+2}-SO$_4^{-2}$-Cl$^-$ and Na$^+$-Cl$^-$-SO$_4^{-2}$. While

cluster analysis can be used to exactly extract clusters and relate to principal components, in our case the commonalities in the clusters obtained from the cluster analysis have been used to relate to the PCA output. More exact relation can probably be obtained by having more explicit details pertinent to the regions geology and lithology which unfortunately is not available for this kind of research from Al-Kharj region, Saudi Arabia so far. Also this paper does not undertake the speciation of arsenic to arsenite As(III) and arsenate As(V) which could have helped in relating the data more to the groundwater chemistry of the region. Also the components PC3, PC4, PC5 can in principle be ignored as they account for mere 10.1%, 8.4%, and 6.5% of the total variance and their eigenvalues are far less than the average of the five eigenvalues.

TABLE 4: Loading of physiochemical parameters in the principal components expressing the geochemical processes.

	PC1	PC2	PC3	PC4	PC5
pH	−0.071	−0.325	0.362	0.117	0.313
TDS	0.361	−0.116	−0.098	−0.013	−0.077
Na^+	0.340	0.041	−0.012	0.175	−0.148
K^+	0.336	0.031	0.210	0.067	−0.054
Ca^+	0.282	−0.253	−0.117	0.003	−0.307
Mg^+	0.360	0.046	−0.067	−0.081	0.024
HCO_3^-	0.155	0.456	−0.105	−0.104	0.273
Cl^-	0.247	−0.301	−0.226	−0.255	0.208
NO_2^-	0.124	0.028	0.551	0.357	0.250
NO_3^-	0.158	−0.445	−0.109	0.129	−0.072
SO_4^-	0.355	0.050	0.058	0.072	−0.126
TOC	0.185	0.416	−0.087	−0.219	0.278
Mn	0.105	−0.009	0.578	−0.327	−0.109
As	0.145	−0.304	−0.023	−0.381	0.568
Fe	−0.029	0.332	0.265	−0.622	−0.403
B	0.331	0.213	0.057	0.181	−0.020

(a)

(b)

FIGURE 3: Multivariate statistical analysis of Al-Kharj groundwater data: (a) cluster analysis with respect to As and B (b) cluster analysis with respect to Fe, As, Mn, TOC, HNO_3^-.

3.3. Miscellaneous Processes. While reductive dissolution of As from arsenopyrites/Fe oxihydroxides is a biotic process, the competitive effect of direct carbonate ions in ground water is proposed to be another major abiotic process of As release [43]. The bicarbonate exhibits poor correlation with total As concentration indicating that direct competitive effect of bicarbonate on As for adsorbtion site is not a process occurring in As mobilization at Al-Kharj region (Figure 4). The presence of nitrate in anoxic waters is linked to the chemolithotropic dinitrification of arsenite to arsenate. This is believed to facilitate the anoxic oxidation of ferrous iron Fe(II) and the arsenite As(III) to ferric iron Fe(III) and less mobile arsenate As(V) [44]. This process does not appear to be occurring in the largely anoxic sulfidic waters of the Al-Kharj aquifers as nitrate and arsenic do not exhibit a significant negative correlation as would be expected by this process (Figure 4). The nitrate presence should facilitate the process of oxidation of arsenite to arsenate which is relatively less mobile and reprecipitated to the Fe hydroxides, if this process would occur the nitrate correlates negatively to the total As content, but that does not seem to be the case in the Al-Kharj aquifers.

3.4. Geothermometry to Access Correlation of As Release to Temperature Gradient. A direct comparison of the temperature from wellheads has in many cases shown low correlations comparing the arsenic levels with the temperature gradient [13, 16, 45]. And therefore most of the researches have relied on understanding the mobilization of arsenic through hydrogeochemical data, this paper does the same. It can be realized that there are divers geothermometric technique like Na/K geothermometer, Na/Li geothermometer, and SiO_2 geothermometer which are used to assess the exact temperature of geothermal waters at the point of origin, but these techniques depend on the hydrochemical properties and have
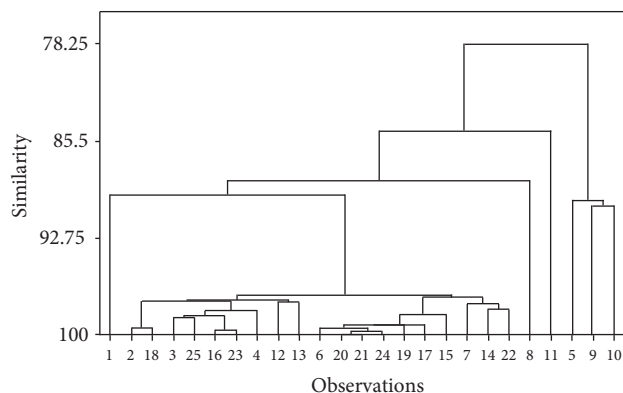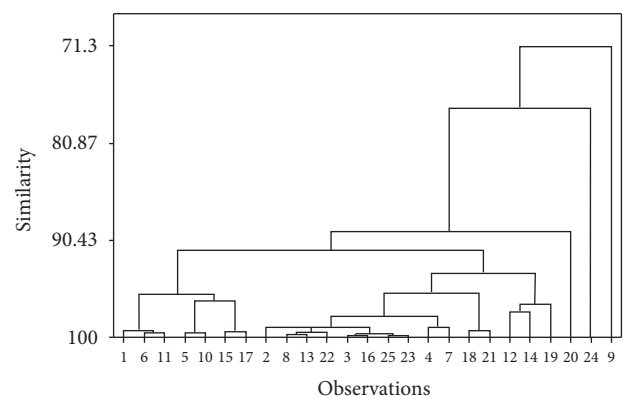
been largely restricted in efficiency of use [46]. Therefore this paper does not attempt to report or enhance on the role of temperature in arsenic mobilization. A more precise hydrochemical characterization of mixing between thermal and nonthermal groundwater as performed by Navarro et al., 2011 and Piqué et al., 2010 is suggested to an enhanced understanding of the geochemistry, geothermal mechanisms, lithology, and geomorphology in Al-Kharj geothermal fields [13, 45].

4. Conclusions

Characterization of hydrogeochemistry and arsenic contamination in geothermal systems of Al-Kharj aquifers in Saudi Arabia has been done to understand the primary processes causing the arsenic mobilization into the groundwater. The main processes responsible are geothermal, and this has been established with different geothermal tracers and geostatistics. The reductive dissolution of arsenic bearing minerals could also be a process occurring, this has been observed and concluded as the aquifer systems in Al-Kharj region show significant amounts of TOC content and experience a slow water moment with low recharge rates, which is why the system has only two major water types classification. The processes
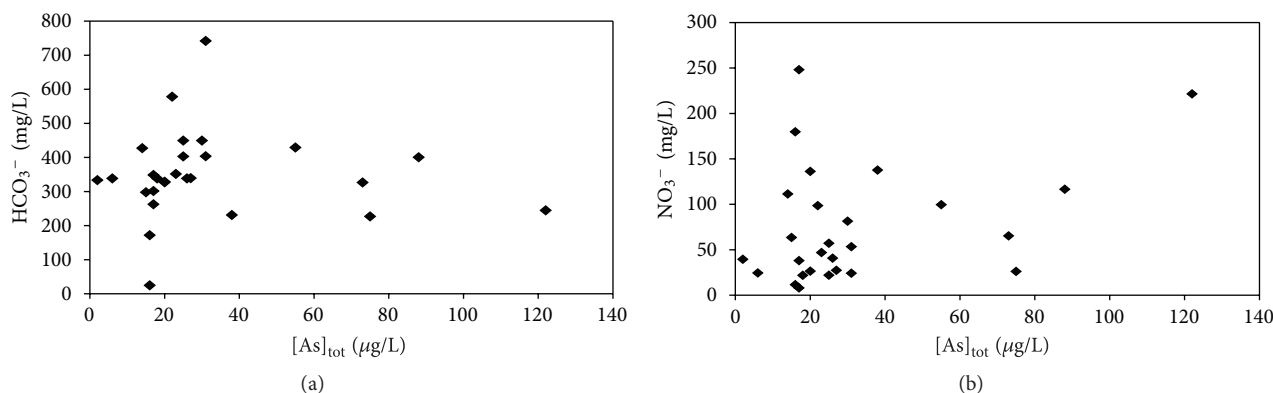
(a)

(b)

FIGURE 4: Bicarbonate and nitrification corresponding to correlation with the total arsenic $[As]_{tot}$ R^2 $(HCO_3^-) = 0.002$; R^2 $(NO_3^-) = 0.120$.

like the mobilization due to competitive effects of carbonate ions to As and chemolithotropic dinitrification of arsenite to less mobile arsenate can be ruled out in this system which is characteristically anoxic and high in sulphate levels. A thorough investigation though is needed to comprehensively study this system which may include profiling mineralogical and morphological patterns of the sedimentary rocks and aquifer system along with hydrogeochemical studies.
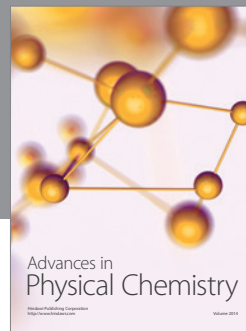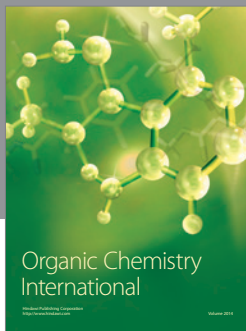
Acknowledgment

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