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Research Article

Assessment of Major and Trace Elements in Drinking Groundwater in Bisha Area, Saudi Arabia

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Drinking groundwater represents 30% of the world's fresh water and 0.9% of the whole world's water. Therefore, routine analysis and monitoring of the groundwater is a paramount issue, specifically the measurement of elemental concentrations due to aquifer characterization. Consequently, the purpose of this study was to determine major and trace elements in groundwater. In total, 25 samples of groundwater were collected from wells in the Bisha area, Asir province, Saudi Arabia. All samples were analyzed for major and trace elements by using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). In total, 15 elements were measured including four major elements (Na, K, Mg, and Ca) and 11 trace elements (V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Cd, and Pb). Major elements (Na, Mg, and Ca) exceeded the guideline limits in some samples. In addition, only one trace element (Se) exceeded the World Health Organization (WHO) permissible limits in some samples. This could be due to rock characteristics in aquifers. Very hard water was shown in 92% of the samples. Moreover, a high percentage (32%) of the analyzed samples also exceeded the guideline levels for chloride. ANOVA analysis showed significant difference ($p < 0.05$) between Bisha samples (North and South), Bisha samples (North), and the remaining samples, for V and pH, and Na, Cl^-, EC, and TDS, respectively. No significant differences ($p > 0.05$) were reported for Na, K, Mg, Ca, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Cd, and Pb between all samples. In general, 25 significant ($p > 0.05$) correlations were reported among the measured elements. For the positive correlations, similar distribution for the elements is anticipated. In conclusion, the groundwater in this study is not suitable for domestic use due to its hardness and only some are suitable for irrigation. More studies are needed to confirm our findings in the study area.

1. Introduction

Groundwater is an important source of drinking water for many countries; high percentages come from groundwater in Saudi Arabia (40%), Denmark (98%), The Netherlands (67%), and Sweden (49%), as reported by UNDEP. Worldwide, there is an increasing trend of using groundwater as a source of drinking water. Therefore, an increasing number of studies have investigated the contamination of groundwater, because groundwater is susceptible to impurities due to its contact with rocks, soil, and plants [1]. Consequently, heavy metals were shown to be the major impurities in groundwater due to the nature of the rocks and weathering phenomena or anthropogenic activities, including the use of fertilizers. All the mentioned parameters could result in serious pollution, which harms human health [2, 3].

Essential and toxic elements are the paramount issues in the investigation of groundwater. The existence of such elements depends on the nature of bedrock and the pH value [4, 5]. The World Health Organization (WHO) [6, 7] set a guideline value of 40 and 10 μg/L in drinking water for essential Se and toxic As, respectively.

Numerous studies have investigated trace elements and other contaminants in groundwater [8, 9]. The presence of radioactive elements was also measured to determine the suitability of groundwater for drinking [10]. A previous study in Saudi Arabia investigated the presence of heavy metals in groundwater and concluded that some samples were not suitable for human consumption [11].

The driving forces behind the investigation of groundwater are the avoidance of ecosystem disturbance and the determination of the causes of contamination, either geogenic or anthropogenic, to allow strategies for remediation to be set. This has raised awareness of the need to stop harmful human activities that had negative impacts on the environment. This has also led to comprehensive studies on the effects of toxic elements such as uranium, which has adverse health effects in humans, especially in the kidneys [12–14]. Most of the studies that investigated uranium in drinking water suggested that the safe range of uranium in drinking water is 2–30 μg/L. Therefore, it is essential to determine the tolerable daily intake (TDI), which refers to the amount that can be consumed every day over a lifetime without significant health risk [15].

The hardness of drinking water has a long history of continuous debate. Different epidemiological studies have shown an inverse relationship between drinking hard water and cardiovascular disease. Therefore, there is no stark evidence to associate the consumption of hard water with health adverse effects. Consequently, no health-based guidelines have been set by the WHO (2003). This leads us to recommend being cautious about the consumption of hard water. Few studies were focused on the evaluation of elements in drinking groundwater in the south area of Saudi Arabia. Previous studies [16–18] were in Najran, Jazan, and Asir (city of Khamis Mushait), respectively. However, no specific study was carried out in the Bisha area. Moreover, the groundwater from wells is the major source of drinking water in the Bisha area. Yet, no studies are available related to the evaluation of Bisha's drinking groundwater. Therefore, the purpose of this study was to assess the major and trace elements in groundwater from the Bisha region.

2. Materials and Methods

2.1. Sample Collection and Preparation. In total, 25 samples were collected from groundwater (wells) in the Bisha area, Asir province, Saudi Arabia (Figure 1). Figure 1(a) shows the whole map of Saudi Arabia including Asir province. Figure 1(b) presents the locations of collected samples. The depth of all wells was between 60 and 70 meters. The samples were collected between July and August 2018. All samples were kept in polyethylene bottles before analysis.

2.2. Measurement of Some Parameters (EC, TDS, and TH) Including Chloride. Electrical conductivity (EC) total dissolved solids (TDS) and pH were measured for all samples at room temperature upon arrival at King Khalid University using an Oakton PC 450 Waterproof Portable Meter. Total hardness (TH) was determined by complexometric titration method. Each water sample was titrated with 0.01 M EDTA disodium, including ammonia buffer (pH = 10) and using Eriochrome Black T as the indicator. 2 mL of the buffer followed by 3 drops of the indicator was added to 25 mL of a sample and then was titrated against the titrant (0.01 M EDTA) until the solution changed from wine red to blue [19]. Chloride concentration was measured by the precipitation titration method (Mohr's method). 25 mL of the water sample was used and a pH was adjusted between 7 and 10; 1 mL of 5% $K_2Cr_2O_4$ was added as an indicator and then titrated against 0.014 M $AgNO_3$ until the solution color was changed to brown-red.

2.3. Elemental Measurement by Using ICP-MS. In total, 15 elements were measured in all collected samples. Concentrations of four major elements (Na, K, Mg, and Ca) and eleven trace elements (V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Cd, and Pb) were measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (iCAP Q, Thermo Fisher Scientific, Waltham, MA, USA) in all 25 samples ($n = 25$). Samples were analyzed in triplicate ($n = 3$). The iCAP Q ICP-MS Thermo Scientific operating conditions were reported by [20].

2.4. Chemicals, Reagents, and Analytical Method. A single-stock solution was prepared from a mixture of 29 elements at a concentration of 10.0 ± 0.05 μg/mL from ULTRA Scientific (North Kingstown, RI, USA). A stock solution (1000 μg/mL) of an internal standard (Sc) was also obtained from ULTRA Scientific (North Kingstown, RI, USA). A stock solution (1 g/L) of an internal standard (Rhodium, Rh) was obtained from AppliChem (Panreac, Germany). Also, a stock solution (1 g/L) of an internal standard (germanium, Ge) was obtained from AppliChem (Panreac, Germany).

Fresh standards for the analysis were prepared daily from stock solutions in 1% HNO_3. A concentration of 100 μg/L of Sc was used as an internal standard for the analysis. Also, concentrations of 20 μg/L of Rh and Ge were used as internal standards for the analysis.

The calibration standards for trace elements (including all fourteen elements) were 5, 10, 20, 50, and 100 μg/L, and for major elements (including all four elements), they were 5, 10, 20, 40, and 80 mg/L.

2.5. Quality Control. The daily performance of ICP-MS in terms of sensitivity and background signals was checked by using a tune solution (B iCAP) containing U, In, Li, and Co, which contained 1 μg/L for each element in 2.0% HNO_3 and 0.5% HCl. Kinetic energy discrimination (KED) mode including helium gas was used.

Limits of detection (LODs) and limit of quantification (LOQ) for all eighteen elements were calculated by measuring the blank (1% HNO_3) ten times, and the standard deviation (SD) was used for calculations as follows: $LOD = 3 \times SD$ and $LOQ = 10 \times SD$. LODs and LOQs were as follows (μg/L): V (0.09 and 0.31), Cr (0.11 and 0.38), Mn (0.11 and 0.37), Co (0.33 and 1.12), Ni (0.71 and 2.38), Cu (0.73 and 2.43), Zn (1.44 and 4.79), As (0.55 and 1.84), Se (1.76 and 5.88), Cd (0.24 and 0.79), and Pb (0.18 and 0.60). For the major elements, they were (mg/L) as follows: Na

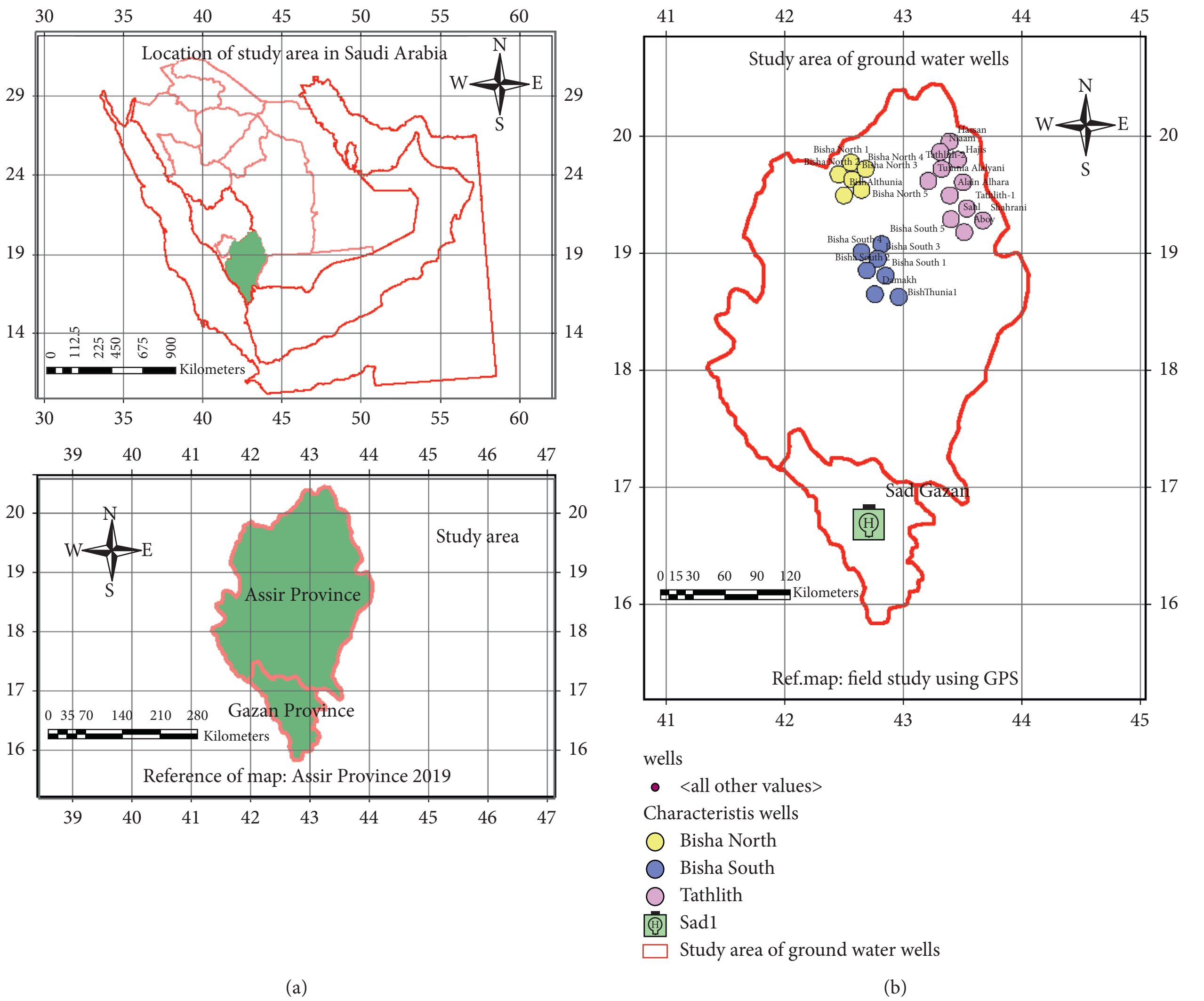

Figure 1: (a) Map of Saudi Arabia including Asir province. (b) Map of Asir province including Bisha region (study area) showing the groundwater sampling locations.

(0.01 and 0.04), K (0.07 and 0.23), Mg (0.01 and 0.02), and Ca (0.41 and 1.36).

A continuing calibration verification (CCV) was also used for a quality control (QC) test for each run. It was performed by measuring 50 μg/L of a mixed standard of all measured elements after each set of ten samples. In the QC, each element was measured three times ($n = 3$). Throughout the whole session, the QC analysis was repeated three times; thus, each element was measured nine times ($n = 9$). The recoveries in one session were as follows: V (97.3%), Cr (96.8%), Mn (99.7%), Co (98.4%), Ni (94.4%), Cu (94.7%), Zn (117.5%), As (99.2%), Se (106.2%), Cd (98.2%), and Pb (98.5%). For the major elements, 40 mg/L of a mixed standard of all four elements was used for CCV, and the recoveries were as follows: Na (112.4%), K (112.1%), Mg (114.9%), and Ca (109%).

2.6. Quality Assurance (QA). The accuracy of the measurement was determined by measuring groundwater certified material (ERM-CA616) from the Institute for Reference Materials and Measurements (IRMM) European Reference Materials (ERM). The results of the measured major elements were similar to those of the ERM-CA616 groundwater. The values for certified (mg/L) and measured (mg/L) groundwater were as follows: Ca (42.6 ± 1.4; 44 ± 2.02), Mg (10 ± 0.3; 10.6 ± 0.11), K (5.79 ± 0.15; 6.05 ± 0.48), and Na (27.9 ± 0.8; 29.55 ± 2.07).

Furthermore, spiked samples were used for QA. For the major elements, 40 mg/L of each element was spiked in a sample and the recoveries were as follows: Ca, 93%; Mg, 101%; K, 96%; and Na, 94.3%. For trace elements, a mixture of 50 μg/L was spiked in a sample and the recoveries were as follows: V (105.8%), Cr (102%), Mn (96%), Co (103.4%), Ni (100.5%), Cu (98.9%), Zn (79.4%), As (102.7%), Se (98.6%), Cd (101.2%), and Pb (79.1%).

2.7. Statistical Analysis. One-way analysis of variance (ANOVA) SPSS version 20 was used to evaluate and to identify significant differences ($p < 0.05$) for values presented for all elements and parameters, measured for all collected water samples from different locations in the Bisha region, with the influence of 95% confidence level. The ANOVA was used to decide whether there were any statistically significant differences between the means of concentrations/values of all measured elements and parameters of all samples from different locations in the Bisha region. The mean difference is significant at the 0.05 level. A correlation analysis was also performed for all 15 measured elements (Na, K, Mg, and Ca, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Cd, and Pb), by using SPSS. This was to establish if there were correlations between every two elements and to explore the strength of such correlations.

3. Results and Discussion

Different parameters were measured in the 25 groundwater samples. EC values range was 124–3140 μS/cm, pH was 6.98–8.06, TDS was 107–5270, and TH range was 124–3140 mg/L, as presented in Table 1. Based on our results reported for the TDS, 28% of samples ($n = 7$) were not suitable for drinking water, because they exceeded the guideline value (1000 mg/L) for TDS set by WHO in drinking water [6]. Moreover, 92% of the samples contained very hard water, because they exceeded the value (180 mg/L), which characterize the hard water.

Table 1 shows that 31.8% of the measured samples exceeded the guideline value (250 mg/L) for chloride in drinking water set by WHO [6]. Contamination of drinking groundwater by chloride is due to some anthropogenic sources of chloride in groundwater which are road salt, animal and human waste, and agricultural activities such as fertilizers [22].

In total, eight samples showed high levels of major elements Na, Mg, and Ca (Table 2). These were collected from Aboy, Hassan, Bisha Thunaia and Damakh, Alaliani, and Sahl. The other two samples from Alain Alhara and Bisha Thunia-1 showed high levels for only Na and for Na and Ca, respectively. The concentrations (mg/L) of Na, Mg, and Ca were as follows: Aboy (947.07, 249.17, and 770.39), Hassan (997.3, 141.56, and 449.29), Bish Thunaia (1093.42, 168.00, and 522.83), Damakh (277.96, 61.05, and 349.05), Sahl (817.14, 155.75, and 521.01), Alaliani (1282.58, 309.24, and 1040.14), Alain Alhara (Na (572.99)), and Bisha Thunia-1 (Na (291.40) and Ca (268.38)).

Concentration levels (μg/L) of all measured trace elements are shown in Table 3 for the 25 collected groundwater samples. The mean concentrations (μg/L) of the trace elements in increasing order were as follows: Co (0.05) < Cd (0.29) < Cu (0.41) < Cr (0.52) < Ni (0.63) < Pb (0.67) < As (0.95) < Mn (1.73) < V (5.23) < Zn (8.38) < Se (24). This is presented in Table 4. Ten trace elements (V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, and Pb) did not exceed the guideline levels set by the WHO [6]. Seven elements (Co, Cd, Cu, Cr, Ni, Pb, and As) had a mean concentration of less than 1 μg/L. However, one trace element (Se) was reported to have a higher level in some samples. In total, nine samples for Se were reported to exceed the guideline levels related to Se (10 μg/L) as shown in Table 3.

Regarding selenium (Se), the five samples that exceeded the guideline value set by the WHO (40 μg/L) were Aboy (152.84 μg/L), Sahl (53.65 μg/L), Hajes (26.57 μg/L), Hassan (55.3 μg/L), Bish Thunaia (72.19 μg/L), Damakh (16.82 μg/L), Alain Alharah (14.21 μg/L), and Shahrani (16.23 μg/L). Another nine samples (Bish1, Bish-2, Bish S3, Bish S4, Bish S5, Tathleeth-1, Tathleet-2, Sadd Jazan, and Bisha Thunaia-1) exceeded the permissible level based on individual drinking three liters per day. Four samples (Aboy, Hassan, Bish Thunaia, and Damakh) had common high levels for Se and the three major elements Na, Mg, and Ca.

SPSS was used as shown in Table 4, to perform a correlation of 15 major and trace elements in 23 samples. 25 significant ($p < 0.05$) correlations were reported. Thirteen and twelve correlations were significant at the 0.01 and at the 0.05 levels, respectively. Three and twenty-two correlations were negative and positive, respectively. All the three negative correlations were related to Vanadium as follows: V/Mn, V/Cu, and V/Zn. The twenty-two positive correlations were thirteen at the 0.01 level (Na/Mg, Na/Ca, Na/Co, Na/Se, Mg/K, Mg/Ca, Mg/Se, Ca/Se, Mn/Cu, Co/Ni, Ni/Pb, and Cd/Pb). The twelve at the 0.05 level were Na/Mg, Mg/Co, K/Cd, Ca/Co, Cr/Cd, Cr/Pb, Co/As, Co/Cd, Ni/As, and negative correlations were V/Mn, V/Cu, and V/Zn. All major elements (Ca, Mg, and Na) had positive correlations with each other and also with Co and Se, except K. Only Mg showed a correlation with K (Mg/K). Remarkably, the two toxic elements Cd and Pb had a significant correlation (Cd/Pb, 0.85^{**}).

ANOVA was performed, by using SPSS (version 20) at a 95% confidence interval to determine the differences among the samples. The differences were related to the levels of variances such as parameters (EC, pH, TDS, and TH) anion (Cl^-), major elements (Na, Mg, Ca, and K), and trace elements (V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Cd, and Pb). All samples were divided into three groups: Bisha South, Bisha North, and the rest of the samples. pH showed a significant difference ($p < 0.05$) between Bisha samples (North and South) and the rest of the group. Among Bisha samples, there was no significant difference ($p > 0.05$). EC and TDS showed a significant difference ($p < 0.05$) between Bisha samples (North) and the rest of the samples. TH showed no significant difference ($p > 0.05$) between all groups. The Cl^- only showed significant differences between Bisha North sample and the rest of the samples. For major elements, only Na showed significant differences ($p < 0.05$) between Bisha North sample and the rest of the samples. However, Ca, Mg, and K showed no significant difference ($p > 0.05$) between all groups. For trace elements, only V showed significant differences. V showed significant differences ($p < 0.05$) between Bisha samples (North and South) and the rest of the samples. For other trace elements (Cr, Mn, Co, Ni, Cu, Zn, As, Se, Cd, and Pb), no significant difference ($p > 0.05$) was reported.

Elements in drinking water are divided into major and trace elements. Trace elements are divided into four ranges based on their availability/concentrations (μg/L): 0.1–1 (V, Se, As, Cd, Co, Ni, Cr, Pb, and Al), 1–10 (Li, Ba, Cu, Mn, and

Table 1: Conductivity, TDS, pH, TH, and chloride concentration for 25 groundwater samples.

Sample no.	Sample name	pH	Conductivity (EC) (μS/cm)	TDS (ppm)	TH	Chloride (ppm)
1	Bisha South 1	7.71	936	468	286	132.93
2	Bisha South 2	7.86	605	302	262	110.36
3	Bisha South 3	7.93	914	457	280	125.40
4	Bisha South 4	7.95	909	454	250	120.39
5	Bisha South 5	7.89	721	360	262	110.36
6	Bisha North 1	8.06	400	200	160	45.15
7	Bisha North 2	8.01	422	211	186	57.69
8	Bisha North 3	8.06	427	223	224	50.16
9	Bisha North 4	8.04	445	222	250	50.16
10	Bisha North 5	8.04	430	215	200	40.13
11	Hassan	7.25	6370	3200	1200	737.37
12	Hajis	7.56	2080	1040	1000	*
13	Niaam	7.59	452	226	404	115.37
14	Tathlith-2	7.2	1345	602	504	150.48
15	Alalyani	6.98	10430	5270	2980	2558.24
16	Damakh	7.27	3750	1930	928	551.78
17	Sadd Jazan	7.24	1628	814	298	223.22
18	Alain Alhara	7.39	3260	1630	328	506.63
19	Tathlith-1	7.4	1321	661	448	*
20	Tumnia	7.73	212	107	124	50.16
21	Bish Althunia	7.12	820	410	172	*
22	Sahl	7.18	5280	2640	1586	702.26
23	Shahrani	7.2	3280	1600	904	501.62
24	Bisha Thunia 1	7.56	860	415	220	1655.33
25	Aboy	7.23	14760	4670	3140	2758.88
Guideline value#		6.5–9.5	800–2300@	1000	500	250

#Set by WHO [6]. @Set by SASO [21]. *Missed samples.

Table 2: Concentrations (mg/L) of the major elements mean ± SD ($n = 3$), in 23* groundwater samples.

Sample name	Na	Mg	K	Ca
Bisha South 1	65.90 ± 3.02	33.37 ± 0.91	7.23 ± 0.30	75.69 ± 4.15
Bisha South 2	64.46 ± 1.34	35.73 ± 0.67	20.66 ± 1.12	74.41 ± 4.42
Bisha South 4	73.38 ± 1.55	40.06 ± 0.19	9.20 ± 0.79	73.93 ± 4.22
Bisha South 5	72.00 ± 3.41	41.16 ± 4.88	8.75 ± 0.87	74.86 ± 5.54
Bisha North 1	30.40 ± 1.09	12.44 ± 0.92	5.66 ± 0.50	61.40 ± 2.20
Bisha North 2	32.49 ± 1.77	12.83 ± 0.18	5.84 ± 0.46	60.79 ± 2.07
Bisha North 3	30.95 ± 0.11	12.31 ± 0.13	5.68 ± 0.15	57.77 ± 1.16
Bisha North 4	31.21 ± 0.86	12.69 ± 0.52	5.65 ± 0.27	58.10 ± 2.83
Bisha North 5	8.04 ± 0.59	430.00 ± 0.57	215.00 ± 0.17	200.00 ± 2.19
Hassan	997.34 ± 19.35	141.56 ± 8.57	4.37 ± 0.26	449.29 ± 20.73
Niaam	42.61 ± 1.20	9.02 ± 0.53	5.14 ± 0.19	58.10 ± 1.87
Tathlith-2	79.82 ± 4.82	47.25 ± 4.14	9.40 ± 0.84	161.14 ± 17.36
Alalyani	1282.58 ± 118.46	309.24 ± 28.59	11.00 ± 1.36	1040.14 ± 103.30
Damakh	277.96 ± 12.74	61.05 ± 1.40	9.69 ± 0.24	349.05 ± 18.81
Sadd Jazan	158.64 ± 3.90	26.95 ± 1.80	10.84 ± 0.64	95.63 ± 3.13
Alain Alhara	572.99 ± 11.73	9.10 ± 0.64	20.48 ± 0.85	142.69 ± 4.91
Tathlith-1	72.27 ± 1.36	40.74 ± 0.82	8.62 ± 0.14	134.79 ± 6.81
Tumnia	12.63 ± 0.39	4.69 ± 0.20	3.07 ± 0.42	35.95 ± 2.38
Bish Althunia	1093.42 ± 10.45	168.00 ± 3.98	9.30 ± 0.13	522.83 ± 8.93
Sahl	817.14 ± 39.53	155.75 ± 8.01	10.37 ± 0.89	521.01 ± 27.21
Shahrani	53.95 ± 3.13	15.60 ± 0.76	6.20 ± 0.26	73.98 ± 2.42
Bisha Thunia 1	291.40 ± 22.59	93.92 ± 6.52	14.30 ± 1.49	268.38 ± 14.18
Aboy	974.07 ± 28.79	249.17 ± 5.89	3.98 ± 0.19	770.39 ± 19.11
Guideline value#	300	30–150&	NA	200&

Two samples were missed. #Set by WHO [6]. &Set by SASO [21].

U), 10–100 (P, B, Fe, and Zn), and 100–1000 (Sr). The major elements (mg/L) are divided into three ranges based on their concentrations: 1–10 (Mg, K, and Si), 10–100 (Na and Ca), and >100. Further, these elements are divided into essential (Se, Mn, Fe, Cu, Ni, Co, Cr, V, Li, P, Sr, Mg, K, Na, and Ca) and toxic elements (As, Cd, Pb, Al, U, and B) [23].

Table 3: Concentrations (μg/L) of the 15 elements measured in 25 samples of groundwater ($n = 3$; mean ± SD).

Sample name	V	Cr	Mn	Co	Ni	Cu	Sample name	Zn	As	Se	Cd	Pb
Bish S 1	6.19 ± 0.19	0.46 ± 0.06	0.32 ± 0.04	0.04 ± 0.00	0.33 ± 0.01	0.24 ± 0.01	Bish S 1	2.92 ± 0.15	0.88 ± 0.09	4.32 ± 0.41	0.04 ± 0.01	0.25 ± 0.00
Bish S 2	6.21 ± 0.09	0.46 ± 0.02	0.43 ± 0.03	0.04 ± 0.01	0.36 ± 0.02	0.24 ± 0.00	Bish S 2	3.16 ± 0.09	0.76 ± 0.01	4.26 ± 0.25	0.19 ± 0.04	0.33 ± 0.02
Bish S 3	6.05 ± 0.07	0.49 ± 0.01	0.26 ± 0.07	0.03 ± 0.01	0.38 ± 0.02	0.18 ± 0.01	Bish S 3	3.14 ± 0.09	0.83 ± 0.13	4.18 ± 0.19	0.07 ± 0.04	0.29 ± 0.03
Bish S 4	6.25 ± 0.14	0.47 ± 0.03	0.50 ± 0.04	0.05 ± 0.00	0.39 ± 0.03	0.23 ± 0.02	Bish S 4	3.16 ± 0.12	0.79 ± 0.08	4.08 ± 0.51	0.04 ± 0.00	0.35 ± 0.01
Bish S 5	6.29 ± 0.19	0.49 ± 0.02	0.34 ± 0.04	0.03 ± 0.01	0.36 ± 0.05	0.20 ± 0.01	Bish S 5	3.30 ± 0.24	0.86 ± 0.08	4.79 ± 0.57	0.04 ± 0.01	0.31 ± 0.02
Bish N 1	6.71 ± 0.21	0.76 ± 0.00	1.32 ± 0.05	0.08 ± 0.01	1.09 ± 0.03	0.45 ± 0.02	Bish N 1	7.42 ± 0.26	0.99 ± 0.09	2.83 ± 0.42	0.49 ± 0.03	0.98 ± 0.01
Bish N 2	6.75 ± 0.17	0.56 ± 0.02	0.45 ± 0.01	0.03 ± 0.00	0.40 ± 0.03	0.21 ± 0.02	Bish N 2	3.71 ± 0.36	0.99 ± 0.08	2.37 ± 0.20	0.10 ± 0.01	0.31 ± 0.01
Bish N 3	6.79 ± 0.06	0.56 ± 0.02	0.51 ± 0.01	0.03 ± 0.01	0.38 ± 0.04	0.20 ± 0.00	Bish N 3	3.74 ± 0.32	1.05 ± 0.03	2.92 ± 0.09	0.07 ± 0.01	0.28 ± 0.01
Bish N 4	6.75 ± 0.27	0.62 ± 0.04	0.75 ± 0.06	0.04 ± 0.01	0.49 ± 0.04	0.28 ± 0.02	Bish N 4	4.06 ± 0.05	0.99 ± 0.09	2.47 ± 0.44	0.19 ± 0.01	0.54 ± 0.02
Bish N 5	6.70 ± 0.15	0.71 ± 0.07	1.06 ± 0.02	0.06 ± 0.01	0.79 ± 0.09	0.34 ± 0.04	Bish N 5	6.88 ± 0.16	0.95 ± 0.02	2.12 ± 0.57	1.15 ± 0.06	1.24 ± 0.04
Hassan	3.76 ± 0.12	0.79 ± 0.04	0.69 ± 0.05	0.07 ± 0.01	0.59 ± 0.03	0.47 ± 0.03	Hassan	23.81 ± 0.95	1.23 ± 0.02	55.30 ± 1.44	0.23 ± 0.02	0.31 ± 0.01
Hajes	4.25 ± 0.07	0.22 ± 0.03	0.25 ± 0.03	0.03 ± 0.00	0.34 ± 0.05	0.14 ± 0.03	Hajes	2.56 ± 0.18	1.16 ± 0.02	26.57 ± 2.08	0.02 ± 0.01	0.26 ± 0.00
Niaam	0.84 ± 0.04	0.24 ± 0.01	0.75 ± 0.05	0.04 ± 0.00	1.04 ± 0.04	0.36 ± 0.02	Niaam	63.92 ± 2.27	0.68 ± 0.04	2.96 ± 0.13	0.19 ± 0.02	0.34 ± 0.01
Tathlith-2	5.58 ± 0.17	0.38 ± 0.02	0.38 ± 0.03	0.03 ± 0.00	0.81 ± 0.04	0.44 ± 0.01	Tathlith-2	5.69 ± 0.35	0.73 ± 0.05	6.20 ± 0.45	0.09 ± 0.01	0.38 ± 0.02
Alalyani	6.94 ± 0.14	0.25 ± 0.02	0.65 ± 0.04	0.07 ± 0.00	0.63 ± 0.01	0.25 ± 0.03	Alalyani	2.88 ± 0.12	0.28 ± 0.02	121.13 ± 2.95	0.14 ± 0.01	0.35 ± 0.01
Damakh	3.52 ± 0.07	1.03 ± 0.07	0.35 ± 0.01	0.06 ± 0.01	0.43 ± 0.03	0.20 ± 0.02	Tathlith-1	9.20 ± 0.87	0.67 ± 0.05	6.16 ± 1.15	0.14 ± 0.02	0.42 ± 0.01
Sad Jazan	2.76 ± 0.08	0.23 ± 0.03	0.60 ± 0.06	0.06 ± 0.01	0.87 ± 0.01	0.79 ± 0.01	Sad Jazan	4.03 ± 0.18	0.84 ± 0.06	7.79 ± 0.89	0.10 ± 0.02	0.31 ± 0.01
Alainlhara	0.44 ± 0.07	0.30 ± 0.01	28.88 ± .61	0.06 ± 0.00	0.86 ± 0.01	2.67 ± 0.11	Alainlhara	11.39 ± 0.57	1.53 ± 0.09	14.21 ± 0.04	0.09 ± 0.03	0.98 ± 0.10
Tathlith-1	5.52 ± 0.07	0.42 ± 0.02	0.61 ± 0.02	0.04 ± 0.01	0.53 ± 0.01	0.25 ± 0.01	Tamnia	8.17 ± 0.06	0.07 ± 0.03	2.47 ± 0.04	0.29 ± 0.04	0.41 ± 0.00
Tumnia	0.61 ± 0.02	0.22 ± 0.01	0.59 ± 0.01	0.03 ± 0.00	0.53 ± 0.02	0.21 ± 0.02	Damakh	5.30 ± 0.47	1.56 ± 0.05	16.82 ± 1.78	0.18 ± 0.03	0.38 ± 0.01
Bishthunia	11.6 ± .52	0.37 ± 0.04	0.20 ± 0.03	0.05 ± 0.00	0.38 ± 0.03	0.21 ± 0.02	Bishthunia	6.29 ± 0.22	0.55 ± 0.04	72.19 ± 1.28	0.05 ± 0.02	0.32 ± 0.01
Sahl	4.07 ± 0.17	0.26 ± 0.02	1.08 ± 0.01	0.08 ± 0.00	1.65 ± 0.04	0.82 ± 0.04	Sahl	10.62 ± 0.42	2.19 ± 0.15	53.65 ± 2.06	0.48 ± 0.02	1.91 ± 0.00
Shahrani	3.89 ± 0.18	0.44 ± 0.01	0.30 ± 0.03	0.02 ± 0.00	0.48 ± 0.07	0.15 ± 0.01	Shahrani	4.72 ± 0.03	0.49 ± 0.06	16.23 ± 0.69	0.71 ± 0.18	0.50 ± 0.01
Bishthunian-1	7.10 ± 0.12	1.14 ± 0.07	1.64 ± 0.12	0.09 ± 0.01	0.92 ± 0.02	0.37 ± 0.02	Bishthunian-1	5.42 ± 0.12	1.23 ± 0.06	7.32 ± 0.59	1.84 ± 0.07	3.55 ± 0.01
Aboy	5.13 ± 0.03	1.03 ± 0.02	0.43 ± 0.02	0.06 ± 0.00	0.80 ± 0.06	0.22 ± 0.02	Aboy	3.89 ± 0.09	1.47 ± 0.07	152.84 ± 5.11	0.37 ± 0.07	1.40 ± 0.03
Guideline value[#]	NA	50	400	NA	70	2000	Guideline value[#]	3000	10	40	3	10

[#]Set by WHO [6, 7].

Table 4: Correlation coefficients of 15 major and trace elements of the 23[$] groundwater samples.

Elements	Na	Mg	K	Ca	V	Cr	Mn	Co	Ni	Cu	Zn	As	Se	Cd	Pb
Na	1.00														
Mg	0.54*	1.00													
K	−0.15	0.69**	1.00												
Ca	0.92**	0.69**	−0.02	1.00											
V	−0.08	0.28	0.18	0.12	1.00										
Cr	0.09	0.23	0.13	0.18	0.40	1.00									
Mn	0.17	−0.13	0.03	−0.06	−0.45*	−0.18	1.00								
Co	0.56**	0.44*	0.13	0.53*	0.08	0.40	0.15	1.00							
Ni	0.32	0.23	0.09	0.27	−0.26	−0.10	0.17	0.62**	1.00						
Cu	0.23	−0.11	0.02	−0.03	−0.51*	−0.27	0.95**	0.28	0.38	1.00					
Zn	0.02	−0.10	−0.06	−0.08	−0.54*	−0.21	0.05	0.01	0.35	0.09	1.00				
As	0.34	0.12	0.01	0.22	−0.01	0.40	0.29	0.52*	0.49*	0.40	−0.03	1.00			
Se	0.88**	0.59**	−0.13	0.92**	0.05	0.17	−0.05	0.37	0.20	−0.04	−0.07	0.19	1.00		
Cd	−0.02	0.38	0.44*	0.08	0.21	0.51*	−0.09	0.48*	0.34	−0.09	−0.05	0.14	−0.04	1.00	
Pb	0.21	0.29	0.17	0.23	0.16	0.48*	0.12	0.66**	0.56**	0.16	−0.08	0.47*	0.15	0.85**	1.00

[$]Two samples were missed. *Correlation is significant at the 0.05 level (2-tailed). **Correlation is significant at the 0.01 level (2-tailed).

Overall, a mean of 78.95% of the measured trace and major elements was within the expected ranges (as mentioned above). This is a promising result that shows that the majority of the measured elements are within the acceptable range in drinking water. The investigated groundwater samples in this study were shown to be sources of major and trace elements. Se was reported to have the highest concentrations among the trace elements in the five groundwater samples. Therefore, 20% of the collected samples were not suitable for drinking because of the high level of Se. Four samples had high levels of Se and contained Na, Mg, and Ca: Aboy, Hassan, Bisha Thunia-1, and Damakh. This means that besides naturally occurring elements, these samples were shown to have high water hardness as well.

3.1. Sodium. The guideline for sodium in drinking water is 200 mg/L by WHO [6]. However, there is no health effect associated with a specific high level of ingested sodium for humans. Previous cases reported health effects related to the overdose of sodium chloride, which included vomiting, nausea, convulsions, cerebral effects, pulmonary oedema, and muscular twitching [24]. In addition, it was also reported that the ingestion of a high level of sodium in drinking water and the intake of excessive salt could seriously worsen chronic congestive heart failure. A study by [25] investigated the presence of a high level of sodium in drinking water and its relationship with high blood pressure. The study investigated two communities with similar socioeconomic parameters and exposed them to sodium in drinking water—one group was exposed to 405 mg/L and the other group was exposed to 5 mg/L. The study concluded that there was no significant difference in systolic blood pressure between groups, but there was a significant difference in diastolic blood pressure.

The sodium adsorption ratio (SAR) was calculated as shown in (1) [26] to determine the suitability of the groundwater in this study either for drinking or for irrigation. The range of SAR was between 2.31 and 65.77 large. Many samples (26.1%) had SAR values of >26, which is not suitable for irrigation because SAR values of up to 18 are safe for irrigation [27, 28].

$$\mathrm{SAR} = \frac{\mathrm{Na}^{+}}{\sqrt{1/2\left(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}\right)}}. \quad (1)$$

3.2. Water Hardness: Magnesium and Calcium. Water hardness is defined as the capacity of water to react with soap to produce lather. Further, water hardness can be temporary (carbonate) or permanent (noncarbonate). The water hardness is expressed as mg/L calcium carbonate. Water hardness is mainly defined by the presence of Ca and Mg salts. Nevertheless, other cations contribute to water hardness, such as Al, Mn, Zn, Br, Sr, and Fe. The water hardness is classified into four classes based on $CaCO_3$ concentration (mg/L): below 60 (soft), 60–120 (moderately hard), 120–180 (hard), and higher than 180 (very hard) [29].

There is no clear evidence that water hardness can cause a diverse health effect on humans. Previous studies appeared to show an opposite casual association between water hardness and human health, specifically cardiovascular disease [30, 31, 32]. In contrast, other studies showed adverse health effects related to water softness (less than 75 mg/L), which affects the mineral balance [33]. Therefore, there is an ongoing debate about the protective effect of water hardness and/or magnesium related to cardiovascular mortality. Numerous epidemiological studies have demonstrated a relationship between water hardness and reproductive failure, cardiovascular disease, and growth retardation. Absorption of magnesium and calcium in the renal tubules is caused by acidic water [34]. Accordingly, people must be cautious when drinking hard water due to the ambiguity surrounding the relationship between some diseases and drinking hard water. The effect of water softness and hardness on human health seems to be connected with the well-known ecological law of optimum according to which both extremely high and unusually low levels of these or that parameter are harmful to living beings.

Regarding magnesium, four samples (Aboy, Sahl, Bisha Thunia-1, and Alalyani) had higher concentrations than 150 mg/L (30–150 mg/L), the value that was set by Saudi Arabian Standards Organization [29]. The values were in the range of 155.75 to 309.25 mg/L. Regarding calcium, seven samples (Aboy, Sahl, Hassan, Bisha Thunia, Damakh, Alalyani, and Bisha Thunia-1) had higher concentrations than 200 mg/L; this value was set by WHO [35]. The values for the abovementioned seven samples were in the range from 220 to 3140 mg/L, which exceeds the permissible value.

Total permanent hardness is the sum of calcium hardness plus magnesium hardness, which is the concentration of calcium and magnesium ions and is equivalent to mg/L $CaCO_3$. We found that 92% of our samples contained very hard water—higher than 180 mg/L. The water hardness was determined by titration, as detailed in Section 2.1.

3.3. Selenium. Nine samples (36%) exceeded the guideline value (40 μg/L) set by the WHO [7]. The levels (μg/L) of selenium in the samples were presented in Table 4 for the following samples: Aboy, Sahl, Hajes, Hassan, Bish Thunaia-1, Damakh, Alain Elharah, Alalyani, and Shahrani (Table 4). The rest of the samples were in the range of 2.12 to 7.79 μg/L, and the mean value for the 25 samples was 23.85 μg/L.

Se is abundant in clay-rich sedimentary rocks (shales and mudstone) due to its affinity for clay minerals [36, 37]. The existence of Se in groundwater is due to the mobilization of selenium by irrigation or rainwater from selenium-rich soils and bedrock [38, 39]. Exposure to a high level of selenium causes a decrease in sperm count, an increase in abnormal sperm, and disturbance of the menstrual cycle in monkeys. However, there is no evidence that it causes any changes in other mammals or the human reproductive system. Redundant selenium that enters the human body will be excreted in feces and urine. Nevertheless, exposure to a high level will cause the chemical form of selenium to build up in the human body. Mainly, selenium builds up in the lungs, liver, kidneys, testes, heart, and blood [40]. A recent study [41] was performed on groundwater from Makkah, Saudi Arabia, in 168 wells. Their results showed a selenium range of 3.12–22.22 μg/L, with a mean of 11.08 μg/L. They reported that 61% of their samples exceeded the WHO guideline value. Therefore, their results showed a higher percentage of samples exceeding the guideline value compared with our results. A previous study [42] investigated the concentrations of arsenic, antimony, and selenium in 49 samples of groundwater from the western region of Poland. They reported less than 0.15 μg/L for selenium and concluded that the presence of selenium is due to geogenic factors.

Table 4 presented 25 significant correlations for measured elements among all investigated samples. Major elements (Na, Ca, and Mg) were correlated together except K. The three major elements showed a correlation with only Co and Se, which means that they have a similar distribution in the investigated samples. pH and V showed a significant difference ($p < 0.05$) between Bisha samples (North and South) and the rest of the samples. The Bisha (North) samples were significantly different ($p < 0.05$) from the rest of the samples for EC, pH, TDS, and TH and Cl^-. Fourteen elements Na, K, Mg, Ca, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Cd, and Pb showed no significant differences ($p > 0.05$) among the investigated samples. This indicates that their mean concentrations had no significant difference ($p < 0.05$) between the investigated samples.

4. Conclusions

Regarding trace elements, 36% of the samples exceeded the guideline value set by the WHO for Se. For the major elements, there were eight, six, and seven samples that exceeded the guideline values for Na, Mg, and Ca, respectively. A high percentage (92%) of samples showed very hard water, and one sample was moderately hard. Therefore, the groundwater in this study is not suitable to be used for drinking due to water hardness. In addition, based on SAR values, 26.1% of all samples are not even suitable for irrigation. Moreover, high percentages (32%) of the measured samples are not potable due to high levels of chloride. A 25 significant ($p < 0.05$) correlations were reported among both major and trace elements. Major elements (Ca, Mg, and Na) had positive correlations among each other and two trace elements (Co and Se), except K, which had only one correlation with Mg. We conclude that these three major elements had a similar distribution in investigated samples. Noticeably, both toxic elements Cd and Pb had high significant correlation at the 0.01 level. A significant ($p < 0.05$) negative correlation was reported for V/Mn, V/Cu, and V/Zn, which means that these elements were inversely distributed in the studied samples. From ANOVA analysis, Na, Cl^-, EC, and TDS showed a significant difference ($p < 0.05$) between Bisha samples (North) and the remaining samples. Only V and pH showed a significant difference ($p < 0.05$) between Bisha samples (North and South) and the remaining samples. No significant differences ($p > 0.05$) were reported for Na, K, Mg, Ca, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Cd, and Pb between all samples. We conclude that there were no significant differences between the means of concentrations of these fourteen measured elements of all samples from different locations in Bisha region. Large numbers of samples are needed to endorse our outcomes in the study region.

Data Availability

The data used to support the findings of this study will be provided upon request.

Conflicts of Interest

The authors declare no conflicts of interest.

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