Global NEST Journal, Vol 15, No 3, pp 374-383, 2013

QUALITY ASSESSMENT OF GROUNDWATER OF ALMADINAH ALMUNAWARAH CITY

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Received: 29/08/12
Accepted: 15/04/13

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ABSTRACT

Renewable water resources in Saudi Arabia are limited with groundwater as the major source for water supply. This study was conducted to assess the quality of groundwater in Almadinah Almunawarah, Saudi Arabia. Water samples were collected from 60 wells in 2010. Physical and chemical parameters were examined. The results of colour, turbidity, odour, pH, and nitrite in all samples were below the local drinking water guideline values. The fluoride concentrations in 8% of the samples were higher than the guideline value. The taste in 87% of the samples was unacceptable. Intolerable levels of both total hardness and TDS were found in most of the samples (~ 83%). Nitrate levels were above the guideline value in 65% of sample. Most of the samples (80–87%) have failed the guidelines for sodium, chloride, and sulfate. On the other hand, none of the samples was found to contain Cr, Ni, Cu, Zn, Cd, Ba, and Pb exceeding the guideline values. However, 5% of the samples have As concentrations over the limit (results 12.0–29.0 μg L^{-1}). Similarly, 5% of the samples have Fe concentrations (320–589 μg L^{-1}) in excess of the guideline value. The level of Mn in only one sample (183 μg L^{-1}) was greater than the guideline value and 10% of the samples have Mg (range 159000–210000 μg L^{-1}) above the limit. Although the water of the investigated wells does not satisfy many of the general drinking water guidelines due to the local environment and climate, most of the samples are in compliance with the guideline values for metals in drinking and irrigation water.

KEYWORDS: metals; water quality parameters; arid environment; Saudi Arabia.

INTRODUCTION

The aim of this work is to assess the chemical and physical quality of the groundwater in the city of Almadinah Almunawarah in Saudi Arabia.

The Arabian Peninsula is located in southwest Asia; a region that is distinguished by its aridity and dry environment along with very limited natural fresh water resources (Alhumoud *et al.*, 2010; Alsharhan *et al.*, 2001; Assubaie, 2011 in press; Haddadin, 2002). However, the region is rich in petroleum and mineral resources and has therefore hosted massive related industries which have a great potential to impact the quality of natural water resources (Sadiq and Alam, 1997; Sharma and Al-Busaidi, 2001). During the last fifty years, the region has experienced rapid industrial and economic developments accompanied by a large increase in the number of population which resulted in a higher demand on freshwater, mainly for human consumption and agricultural activities (Al-Senafy and Abraham, 2004; Husain *et al.*, 1991; Murad and Krishnamurthy, 2004). As a consequence, the assessment of the quality and quantity of such limited water resources becomes an imperative tool to manage these resources in the best possible manner for any future sustainable development.

MATERIALS AND METHODS

Study area

Almadinah Almunawarah (elevation 600–630 m, latitude: 24 28N, longitude: 39 36E) is a historical city located in Hejaz region in the north-western part of the Kingdom of Saudi Arabia (KSA) and it is located 190 km away from the Red Sea. The area of the City is about 600 km^2 and its population according to the 2010 census is more than 1.1 million. Due to its religious significance, the City is distinguished by receiving a huge number of pilgrimages and visitors every year. In 2011 for instance, the number of visitors has exceeded 8 million from all parts of the world and this number is expected to double in the coming years. The average annual low and high temperatures for 2011were 12–29 and 22–41 ℃, respectively. The highest recorded temperature in the same year was 47 ℃ (June - August) and the lowest was 1 ℃ (December - March). The City experiences irregular rainfalls, mainly in Winter and early Spring with an average rainfall of about 50 mm. However, the neighbouring areas receive more frequent and heavier rainfalls (up to 200 mm) (Weatherbase).

The City is located on a flat mountainous plateau and surrounded by a number of volcanic mountains from the north and southwest sides and the soil surrounding it is mostly basalt. It has several dry springs and valleys, which used to be rivers during the rainy ages. Among these important valleys (wadis) are Wadi Al-'Aqeeq, Wadi But'haan, Wadi Mahzoor, Wadi Mudthaineeb, Wadi Qunaah, and Wadi Raanoonaa (Almadinah Almunawarah Encyclopedia).

Due to its location in arid environment, its natural geography, and scarcity of rainfall especially in later decades, the area currently lacks major water bearing aquifers (Al-Harbi *et al.*, 2006). The groundwater in the city (depth 15 – 200 m) is mainly charged by local damps, mostly after rainy seasons (Saudi Arabia Ministry of Economy and Planning, 2004). Therefore the groundwater is almost the single source for irrigation in the area. Irrigation water is obtained through dug wells in farms. The number of water wells in the study area (inside the 3rd Ring Road) is about 800 wells. However, treated domestic wastewater is also used for irrigation in Al-Khlail wadi at the northern part of the city (Shraim *et al.*, 2011). During the last 20 years, the city starts to rely on seawater desalinations to face the increased demand on fresh water. Nowadays, the major source of domestic water for the city is desalinated water that is pumped from Yanbu Power and Desalination plant at the Red Sea. However, this water is sometimes partially mixed with local groundwater inside the city. Although the desalinated water is the main source of domestic supply, bottled water produced by private treatment factories from local groundwater wells is largely consumed by the residents and visitors of the city. Additionally, groundwater is sometimes used by farmers and residents of many villages for drinking and cooking, often, without any pretreatment. These reasons necessitate regular assessment and monitoring studies for the groundwater so as to provide accurate data about this valuable water resource.

The locations of investigated groundwater wells are shown in Figure 1.

Chemicals and solutions

All reagents and standards were prepared in ultra-pure water (18.2 MΩ cm, Milli-Q Gradient from Millipore, USA). Nitric acid (90% fuming) was obtained from Fisher Scientific (New Jersey, USA), ICP-MS multi-element calibration standards from Agilent (10 μg mL^{-1} each (USA), analytical reference material (TM-26.3) from Environment Canada, and certified wastewater from High-Purity Standard (CWW-TM-D, 20 μg Hg L^{-1}, Charleston, USA).

Equipment

An Inductively Coupled Plasma Mass Spectrometer (ICP-MS, 7500cx, Aglinet Technologies, Japan) was used for metals analysis. The operational parameters applied were listed elsewhere (Shraim *et al.*, 2011). A Flame Photometer (PFP7, Jenway LTD, Felsted, England) was employed for sodium measurements. Residual chlorine, fluoride, nitrate, nitrite, phosphate, and sulfate were analysed using a DR2000 spectrophotometer (Hach Company, Loveland Colo USA). Hardness and chloride measurements were carried out using a digital titrator (Hach Company). Total dissolved solids (TDS) were measured using a conductivity meter (CO150, Hach Company, Loveland Colo, USA) and finally, pH measurements were performed using a pH meter (HANNA 211, Mauritius, Portugal).

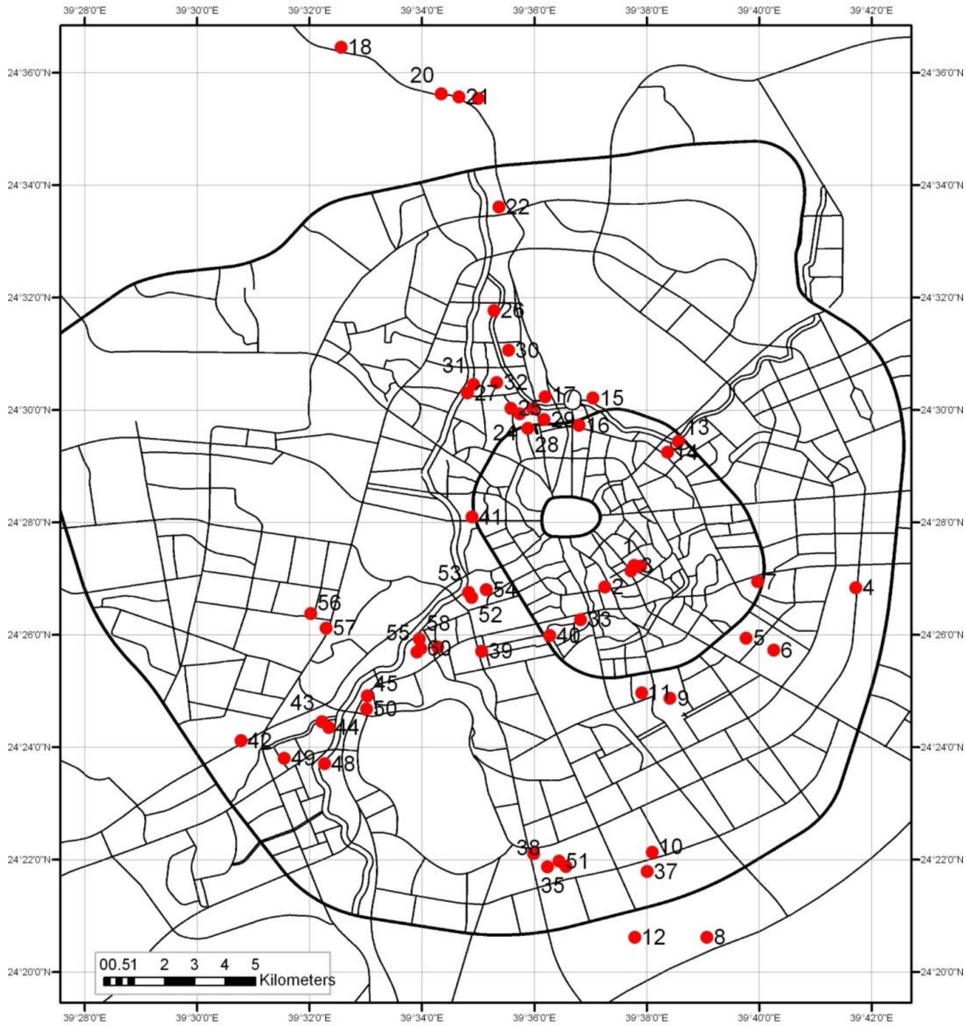

Figure 1. Locations and numbers of sampled water wells in Almadinah Almunawarah city

Samples collection and analysis

Sixty groundwater samples were collected from wells inside the city in June and July, 2010 (see Figure 1). Samples were collected directly from the wells in 10 L clean polyethylene bottles after about 10 min of initial pumping. Collected samples were transported to the laboratory within 2–3 hours after collection without any onsite pre-treatment. Upon arrival to the laboratory, each sample was split into 3 parts: the first one was used for metals and total hardness analyses; the second one was used for phosphate and the sum of nitrate and nitrite analyses; whereas the last part was used for TDS, nitrite, chloride, fluoride, and sulfate analyses. Physical parameters (i.e. temperature, pH, turbidity and TDS) were measured immediately after arrival to the laboratory using portions from the third part before refrigeration. The first part was acidified with nitric acid (1+1) to a pH of 2 or less immediately after arrival to the laboratory and stored inside a refrigerator at 4°C until analysed. Metals analysis was carried out within 2 weeks after collection using 0.22 µm filtered undiluted samples. Subsamples of the second part were treated in the same way as the first one, but sulphuric acid (1+1) was used instead of nitric acid. No treatment was done for the samples in the third part other than storing in a refrigerator at dark for 24 hours before analysis.

RESULTS AND DISCUSSION

General quality parameters

The depth of water in the investigated groundwater wells, ranged from 35–160 m (average 89±34 m, median 90 m). Table 1 lists the general quality parameters of the groundwater samples.

The obtained results of colour, turbidity, odour, pH, and nitrite in all samples were below the Saudi Arabian Standards Organisation (SASO) drinking water guideline values. The fluoride concentrations in 5 samples (8%) were above the guideline value (the max detected value was 2.2 mg L^{-1}). The taste in 87% of the samples (n = 52) was not acceptable. High levels of both total hardness and TDS were found in most of the samples (about 83% of the samples failed the guideline values). The measured amounts of nitrate were relatively high with 65% (n = 39) of the sample over the guideline value. Most of the samples (80–87%) have also failed the guidelines for sodium, chloride, and sulfate contents. According to the Water Quality Association, which classifies water based on TDS levels, only 17% of the groundwater samples can be classified as fresh (<1000 mg L^{-1}), 78% as brackish (1000–5000 mg L^{-1}) and only 5% as highly brackish (>5000–15000 mg L^{-1}) (Water Quality Association). The groundwater quality in some parts of the investigated area in this study has been examined by Hashem and Al-Johany in 1994 (Hashem and Al-Johany, 1994). The reported average TDS concentration was 1128 ± 315 mg L^{-1} (median 992, range 800–1728). The average and median concentration values reported in our study are almost double the values reported in Hashem and Al-Johany study. Similarly our results for TDS, sulfate, and chloride are slightly higher than those reported for the groundwater of Wadi Yalamlam basin, which is ~500 km south of Almadinah Almunawarah (mean values for TDS, sulfate, and chloride were 1930 ± 312 mg L^{-1}, 551 ± 135 mg L^{-1}, 758 ± 62 mg L^{-1}, respectively) (Subyani, 2005). Lower nitrate concentrations have been also reported during 1984–1988 for groundwater samples from the western side of KSA with 91% of the samples (n =1659) has nitrate concentrations <45 mg L^{-1}, 7% (n = 131) <46–90 mg L^{-1}, and 2% (n = 29) <91–140 mg L^{-1}. Similarly, 70% of the samples were found to contain TDS values <1500 mg L^{-1} (n = 1266) (Alaa El-Din *et al.*, 1994). On the other hand, slightly higher TDS and nitrate concentrations were reported for some groundwater samples collected from the western area of KSA in 1993 (TDS mean 455 ± 312 mg L^{-1}, range 210–1200 mg L^{-1}, n = 23 and nitrate mean 15.2 ± 7.3 mg L^{-1}, range 0.0–35 mg L^{-1}, n = 23) (Alaa El-Din *et al.*, 1993). Since these parameters are highly affected by dilution factors due to the difference in feeding rates during rainy and dry seasons, this variation is expected because the precipitation was low during the last 5 years. Also, the probable causes for the increase in the levels of dissolved solids in the investigated wells when compared to those reported in the previous studies for the same area would be leaching of soluble salts from the agricultural soil as well as the extensive depletion of groundwater reservoir, mainly for irrigation, along with low recharge rates (Al-Ahmadi and El-Fiky, 2009; Subyani, 2005).

Generally speaking, the groundwater of the investigated wells does not satisfy many of the general SASO drinking water guidelines and therefore needs proper pre-treatment before utilising as drinking water, but such a groundwater can safely be used for irrigation.

Metals

To ensure the quality of the results, various measures have been undertaken including the limit of detection (LOD), calibration verification checks (CVC), and analysis of certified reference materials. The results of these trials are listed in Table 2.

The LOD values for all analysed metals were in the range of 0.011–0.544 µg L^{-1}. The recoveries for the CVC when using a standard solution containing 25.0 µg L^{-1} of each metal prepared from a stock solution different from that used to construct the calibration curves were 94-104%. On the other hand, the obtained metals concentrations for the CRMs were close enough to the certified values with recoveries ranging from 90 to 115% for all certified elements except Pb, where its recovery was 78%.

A summary of metals concentrations in the groundwater samples is presented in Table 3, whereas the detailed values are listed in Table 4. The average, standard deviation, median, and minimum values reported in Table 3 represent only the samples with concentrations ≥ LOD. Most of the samples are in compliance with the SASO and MAW guideline values for metals in drinking and irrigation water, respectively. None of the samples was found to contain Cr, Ni, Cu, Zn, Cd, Ba, and Pb above the guideline values. On the other hand, 3 samples (5%) contained As slightly higher than the guideline value. These samples were GW21, GW22, and GW26 with As concentrations of 13.3 µg L^{-1}, 12.0 µg L^{-1}, and 29.0 µg L^{-1}, respectively. Similarly, the amounts of Fe in 3 samples (GW37, GW48, and GW52, concentrations: 320 μg L^{-1}, 357 μg L^{-1}, and 589 μg L^{-1}, respectively) exceeded the guideline value. Only one sample (GW49) contained Mn (183 μg L^{-1}) over the guideline value. Finally, 6 samples (GW11, GW12, GW35, GW36, GW38, and GW41) were found to have Mg level higher than the guideline value with a range of 165–210 mg L^{-1}.

Similarly, all the groundwater samples examined in this study are in compliance with MAW guidelines for irrigation water except 5 samples (GW29, GW32, GW37, GW38, and GW40), which were found to contain Cr (range 10.5 – 21.4 μg L^{-1}) in excess of the guideline value (i.e. 10 μg L^{-1}).

As there are no current industrials activities in the investigated area, the variations in the amounts of metals could be ascribed to the geological nature of the area. The level of water in wells and the feeding rates might explain the elevated contents of alkaline and alkaline earth metals (e.g., Mg and Ca) and TDS in some samples. There is also possibility that Cr and As could have came from leather industry in the past.

The results of some metals reported in this work are lower than those reported for groundwater samples collected from the same locations about 17 years ago (Hashem and Al-Johany, 1994). The average reported concentrations in this latter study were 38 μg L^{-1} for Co (max 110), 20 μg L^{-1} for Cu (max 40 μg L^{-1}), 106 μg L^{-1} for Fe (max 320 μg L^{-1}), 29.4 μg L^{-1} for Mn (max 70 μg L^{-1}), and 373 μg L^{-1} for Zn (max 530 μg L^{-1}). On the other hand, Pb was below the limit of detection (not specified) and the average Mg concentration was 38.0 mg L^{-1} (max 64.0 mg L^{-1}); both metals have lower average concentrations than those reported in our work. Additionally, the reported concentrations of metals in this work are also slightly lower than those reported for other areas in KSA (Al-Harbi *et al.*, 2006; Assubaie, 2011 in press).

As evident from the findings of this study, most of the samples contain normal levels of metals with only 2-10% of the samples contained unacceptable, but not too high, concentrations of one or more of the following metals: As, Fe, Mn, and Mg. However, the status of these wells with respect to metals content as well as other quality parameters has to be periodically monitored in order to ensure their quality and identifying any sources of contamination if any. Based on these findings and due to the absence of heavy industries that usually contribute to the groundwater metal pollution in the City of Almadinah Almunawarah, it can be claimed that the groundwater in the investigated areas is relatively unpolluted concerning metal contamination. This should be clear when comparing the results of the groundwater samples examined in this work with those affected by industrial activities such as mining and petrochemical industries, which usually contain much higher concentrations of metals and other contaminants. For instance, copper mining and storage of obtained tailings in Sohar, Sultanate of Oman have been shown to result in elevated concentration of TDS (range 1000–55000 mg L^{-1}), Pb (300 μg L^{-1}), Cr (<20 μg L^{-1}), Zn (94000 μg L^{-1}), and Ni (40–1600 μg L^{-1}) (Sharma and Al-Busaidi, 2001). In another study, the groundwater in shallow aquifers underneath industrial activities in the Eastern Province of KSA has been also shown to be highly contaminated due to these activities. The reported mean concentrations of selected elements in the groundwater were 14.07 ± 7.64 μg L^{-1} (range 5.99–37.4, n = 20) for Cr, 88.2 ± 212 μg L^{-1} (range 0.08–1570 μg L^{-1}, n = 104) for Pb,59.3 ± 87.0 μg L^{-1} (range 0.18–552 μg L^{-1}, n = 104) for Mo, 5.05 ± 3.59 μg L^{-1} (range 0.25–20.0 μg L^{-1}, n = 102) for Ni, 23.4 ± 19.6 mg L^{-1} (range 0.16–89.6 mg L^{-1}, n = 104) for Sr, and 70.6 ± 73.4 μg L^{-1} (range 4.25–324 μg L^{-1}, n = 102) for Zn (Sadiq and Alam, 1997). Such has been coused by leachate from industrial dust area, leakages from oil, and fertilizer industries.

CONCLUSION

Due to the policy of the government to keep the city of Almadinah Almunawarah free of heavy industries, the quality of groundwater in the investigated area is relatively good. However, some sort of water treatment is needed before using such wells for drinking purposes. Although most of the investigated wells satisfied the local drinking water guidelines for metals (i.e. only 2-10% of the samples exceeded the guideline value in one or more the following metals: As, Fe, Mn, Mg), more than 75% of the samples can be considered as brackish. On the other hand, the water of most of the investigated wells can be used safely for irrigation purposes. It is recommended that the quality of the groundwater in the city and the surrounding areas are regularly monitored so as any irregularities can be identified early and dealt with in a cost effective manner.

Table 1. Results of water general quality parameters along with local guideline values (the unit of all parameters, except color, turbidity, taste, odor, and pH is mg L^{-1})

	Color (Unit [a])	Turbidity (NTU)	Taste	Odor	pH	TDS	Total Hardness	Nitrite as N	nitrate as N	Fluoride	Sodium	Residual Chlorine	Chloride	Sulfate
Average	2	0.7	not acceptable for 87% of samples	acceptable for all samples	7.41	2328	1051	0.046	80.2	0.89	471	0.016	752	733
Standard Deviation	1	0.2			0.27	1419	697	0.127	69.3	0.43	348	0.008	545	432
Median	2	0.7			7.43	1975	927	0.007	64.0	0.83	385	0.010	625	700
Minimum	0	0.2			6.92	119	56	0.000	3.52	0.01	24	0.010	44	19
Maximum	4	1.2			8.00	6210	3500	0.710	429.0	2.16	1600	0.040	2462	2260
SASO unbottled drinking water guidelines	15	5	acceptable	acceptable	6.5-8.5	1000	500	3	50	1.5	200	0.500	250	250
MAW irrigation water guidelines	colorless	---	---	---	6.0-8.4	---	---	---	10.0	2.0	---	---	---	---

[a] true color unit

Table 2. Quality control results for metals: concentrations in μg L^{-1}, numbers in parentheses are the standard deviations of 3 replicates

	^{24}Mg	^{51}V	^{52}Cr	^{55}Mn	^{56}Fe	^{59}Co	^{60}Ni	^{65}Cu	^{66}Zn	^{75}As	^{88}Sr	^{111}Cd	^{137}Ba	^{205}Tl	^{208}Pb
LOD [a]	0.161	0.043	0.146	0.083	0.544	0.015	0.023	0.097	0.158	0.011	0.059	0.038	0.051	0.027	0.069
CVC 25	24.0 (0.9)	24.2 (0.9)	24.4 (0.3)	24.4 (0.9)	24.1 (0.8)	25.1 (1.2)	24.4 (0.1)	24.2 (0.9)	24.5 (0.3)	24.9 (0.8)	24.4 (0.7)	24.9 (0.7)	24.1 (0.4)	25.2 (1.1)	26.0 (0.8)
CRM TM-26.3, obtained	4270 (97.4)	13.1 (1.3)	11.2 (0.3)	17.1 (0.8)	20.0 (1.9)	8.56 (0.2)	10.3 (0.3)	12.6 (0.8)	58.0 (0.8)	8.10 (0.2)	99.5 (2.1)	8.16 (0.8)	22.5 (2.1)	5.16 (0.3)	8.23 (0.5)
CRM TM-26.3, certified	4173 [b] (156)	12.1	12.3 (4.2)	17.0 (1.8)	21	8.1 (0.9)	10.2 (1.1)	13.4 (1.1)	39[c]	7.9 (0.8)	96	7.1 (0.3)	25 (1.2)	5.2	9.3 (0.7)

[a] LOD: limit of detection (3 × standard deviation of 5–7 blank readings measured at different times during the run).
[b] This value is for Mg in the certified wastewater CWW-TM-D.
[c] No certified value was provided, instead, an information value was used.

Table 3. Summary of metals concentrations (μg L^{-1}, unit for Mg is mg L^{-1}) in the samples

	^{24}Mg	^{51}V	^{52}Cr	^{55}Mn	^{56}Fe	^{59}Co	^{60}Ni	^{65}Cu	^{66}Zn	^{75}As	^{88}Sr	^{111}Cd	^{137}Ba	^{205}Tl	^{208}Pb
% Samples with results >LOD	100	100	67	47	97	82	40	8	58	98	100	8	100	33	97
% Samples with results >SASO guideline value	10.0	---	0.0	1.7	5.0	---	0.0	0.0	0.0	5.0	---	0.0	0.0	---	0.0
Average [a]	74.0	21.4	5.25	10.6	44.4	0.502	0.856	2.72	23.6	2.26	3816	0.785	28.8	0.989	0.957
Standard deviation [a]	53.4	14.8	5.00	35.7	103	0.224	0.918	3.87	33.6	4.37	2639	0.344	27.1	0.116	0.785
Median [a]	68.6	19.6	3.77	1.32	10.2	0.493	0.675	0.759	8.83	1.18	3630	0.807	20.9	0.963	0.590
Minimum [a]	25.6	2.13	0.360	0.080	0.471	0.054	0.064	0.409	0.640	0.090	51.4	0.424	0.522	0.961	0.195
Maximum	210	89.9	21.4	183	589	1.33	4.78	9.53	134	29.0	12200	1.30	116	1.48	3.86
SASO unbottled drinking water guidelines	150	---	50	100	300	---	20	1000	2000	10	---	3	700	---	10
MAW irrigation water guidelines	---	10	10	200	5000	50	20	400	4000	100	---	10	---	---	100

SASO: Saudi Arabian Standards Organisation standard no. 701.
MAW: Ministry of Agriculture and Water, Saudi Arabia.
[a] only samples with concentrations ≥MDL were included in these statistics.

Table 4. Concentrations of metals (μg L^{-1} for all except Mg and Sr which is mg L^{-1}) in the samples rounded to 3 significant digits

Sample ID	^{24}Mg	^{51}V	^{52}Cr	^{55}Mn	^{56}Fe	^{59}Co	^{60}Ni	^{65}Cu	^{66}Zn	^{75}As	^{88}Sr	^{111}Cd	^{137}Ba	^{205}Tl	^{208}Pb
GW 1	78.3	25.6	4.46	0.380	18.9	0.488	<LOD	<LOD	16.1	0.277	1.83	<LOD	14.8	<LOD	0.195
GW 2	79.6	19.7	1.43	0.549	56.0	0.591	0.069	0.698	12.1	1.15	4.09	<LOD	32.8	<LOD	0.581
GW 3	118	24.8	4.00	<LOD	2.10	0.517	0.484	<LOD	0.882	0.339	2.55	<LOD	23.8	<LOD	<LOD
GW 4	29.8	89.9	2.73	<LOD	5.16	0.631	<LOD	<LOD	27.2	7.50	0.863	0.874	7.76	<LOD	3.86
GW 5	95.4	25.3	5.40	<LOD	5.62	0.490	<LOD	<LOD	4.12	0.429	2.25	<LOD	22.7	<LOD	1.29
GW 6	31.4	12.8	0.876	0.650	15.1	0.518	0.209	<LOD	1.40	2.65	1.94	<LOD	17.2	<LOD	0.306
GW 7	35.3	14.4	0.915	<LOD	14.9	0.489	0.780	<LOD	4.27	3.01	2.61	<LOD	17.3	<LOD	1.56
GW 8	85.5	27.0	1.79	0.380	0.471	0.628	<LOD	<LOD	<LOD	1.19	3.58	0.807	23.1	<LOD	3.46
GW 9	77.3	42.4	1.19	0.416	26.7	1.33	0.595	<LOD	<LOD	3.59	3.02	<LOD	19.5	<LOD	0.922
GW 10	103	19.2	2.90	<LOD	17.6	0.500	<LOD	<LOD	11.2	0.490	4.38	<LOD	23.2	<LOD	0.845

<LOD means: concentration is below limit of detection

Table 4 (continued). Concentrations of metals (µg L^{-1} for all except Mg and Sr which is mg L^{-1}) in the samples rounded to 3 significant digits

Sample ID	^{24}Mg	^{51}V	^{52}Cr	^{55}Mn	^{56}Fe	^{59}Co	^{60}Ni	^{65}Cu	^{66}Zn	^{75}As	^{88}Sr	^{111}Cd	^{137}Ba	^{205}Tl	^{208}Pb
GW 11	206	22.7	5.53	<LOD	6.75	0.493	<LOD	<LOD	<LOD	0.364	4.87	<LOD	32.6	<LOD	0.217
GW 12	165	18.4	3.12	0.472	143	0.476	<LOD	0.409	20.2	0.451	5.26	<LOD	30.8	<LOD	0.389
GW 13	109	11.3	0.590	<LOD	<LOD	0.485	<LOD	<LOD	<LOD	0.250	7.46	<LOD	12.3	<LOD	<LOD
GW 14	33.3	44.1	3.54	<LOD	<LOD	0.697	<LOD	<LOD	<LOD	2.87	1.24	<LOD	13.4	<LOD	0.404
GW 15	146	24.1	4.36	<LOD	0.703	0.505	<LOD	<LOD	<LOD	0.387	3.68	1.30	33.7	<LOD	0.276
GW 16	39.9	68.6	7.38	<LOD	9.98	0.523	<LOD	<LOD	122	1.47	0.822	<LOD	9.53	<LOD	0.393
GW 17	83.9	32.5	7.40	<LOD	13.0	0.452	<LOD	<LOD	3.32	0.395	1.35	<LOD	14.9	<LOD	0.398
GW 18	149	19.9	2.60	<LOD	2.09	0.485	<LOD	<LOD	0.959	0.393	5.22	<LOD	21.4	<LOD	0.220
GW 19	75.2	20.3	1.59	0.746	11.2	0.637	<LOD	<LOD	5.32	1.18	4.11	<LOD	32.7	<LOD	0.500
GW 20	73.7	19.8	1.77	<LOD	10.5	0.650	<LOD	<LOD	<LOD	1.22	3.96	<LOD	34.1	<LOD	0.810
GW 21	20.9	4.20	0.360	4.78	12.5	0.615	0.339	<LOD	<LOD	13.3	8.79	0.424	12.0	<LOD	0.389
GW 22	21.9	11.8	0.530	2.45	14.7	0.613	<LOD	<LOD	<LOD	12.0	5.40	<LOD	16.8	<LOD	0.303
GW 23	110	34.8	9.49	<LOD	1.89	0.739	<LOD	<LOD	<LOD	0.152	1.33	<LOD	3.25	<LOD	0.308
GW 24	64.4	12.9	1.70	0.227	17.5	0.483	<LOD	<LOD	4.92	3.43	6.80	<LOD	19.8	<LOD	0.267
GW 25	2.56	21.7	1.22	<LOD	5.45	0.427	<LOD	<LOD	<LOD	7.41	0.385	<LOD	6.26	<LOD	0.467
GW 26	3.54	11.3	0.546	<LOD	4.89	0.422	<LOD	<LOD	31.1	29.0	0.516	<LOD	21.8	<LOD	0.599
GW 27	73.7	32.4	3.02	<LOD	5.22	0.604	<LOD	<LOD	<LOD	0.405	1.73	<LOD	15.6	<LOD	0.256
GW 28	74.7	21.2	5.11	<LOD	4.82	0.552	<LOD	<LOD	<LOD	0.152	1.61	<LOD	21.0	<LOD	0.229
GW 29	113	20.7	11.8	<LOD	4.52	0.447	<LOD	<LOD	<LOD	0.255	3.56	<LOD	40.0	<LOD	0.276
GW 30	54.9	27.0	4.42	1.33	2.98	0.658	<LOD	<LOD	<LOD	0.212	1.03	<LOD	8.35	<LOD	0.298
GW 31	100	19.5	5.63	<LOD	3.25	0.489	<LOD	<LOD	<LOD	0.205	2.93	<LOD	61.7	<LOD	0.258
GW 32	72.8	25.4	10.5	<LOD	5.30	0.584	<LOD	<LOD	2.34	0.175	1.14	<LOD	3.00	<LOD	0.428
GW 33	96.5	16.5	5.98	<LOD	6.44	0.482	<LOD	<LOD	<LOD	0.090	2.12	<LOD	24.4	<LOD	0.250
GW 34	76.2	17.6	9.77	0.080	11.5	0.446	<LOD	<LOD	1.43	0.435	5.79	<LOD	59.9	<LOD	0.281
GW 35	210	14.4	8.99	<LOD	9.06	0.468	<LOD	<LOD	4.81	0.125	4.51	<LOD	11.2	<LOD	0.240
GW 36	209	14.1	8.13	<LOD	8.44	0.467	<LOD	<LOD	6.37	0.181	4.54	<LOD	15.3	<LOD	0.256
GW 37	8.94	36.9	16.5	3.76	320	0.491	<LOD	<LOD	82.9	2.34	0.278	<LOD	5.21	<LOD	1.15
GW 38	196	16.4	18.6	<LOD	25.9	0.586	<LOD	<LOD	8.07	0.151	3.88	<LOD	11.0	<LOD	0.223
GW 39	3.12	2.10	2.65	1.31	39.8	0.555	4.78	9.53	28.0	<LOD	0.051	<LOD	0.522	<LOD	0.550
GW 40	119	41.9	21.4	<LOD	38.1	0.558	<LOD	<LOD	2.50	0.282	2.04	<LOD	2.83	<LOD	0.340
GW 41	159	12.1	<LOD	<LOD	13.2	<LOD	0.850	<LOD	<LOD	1.41	12.2	<LOD	25.5	0.964	1.38

<LOD means: concentration is below limit of detection

Table 4 (continued). Concentrations of metals (μg L^{-1} for all except Mg and Sr which is mg L^{-1}) in the samples rounded to 3 significant digits

Sample ID	^{24}Mg	^{51}V	^{52}Cr	^{55}Mn	^{56}Fe	^{59}Co	^{60}Ni	^{65}Cu	^{66}Zn	^{75}As	^{88}Sr	^{111}Cd	^{137}Ba	^{205}Tl	^{208}Pb
GW 42	30.8	6.10	<LOD	6.37	8.27	<LOD	0.753	<LOD	<LOD	1.64	5.70	<LOD	55.7	0.964	1.51
GW 43	57.8	14.1	<LOD	2.07	261	0.090	0.605	<LOD	12.9	1.58	7.19	<LOD	112	0.962	1.78
GW 44	21.4	7.90	<LOD	0.185	20.3	0.146	0.738	<LOD	38.5	3.06	2.63	<LOD	113	0.962	1.74
GW 45	41.9	8.20	<LOD	0.278	16.0	0.055	0.777	<LOD	8.83	1.39	5.94	0.521	116	0.963	1.54
GW 46	24.7	8.40	<LOD	2.16	170	0.054	0.416	<LOD	90.2	1.77	4.39	<LOD	50.7	0.961	1.64
GW 47	52.1	6.40	<LOD	2.90	115	<LOD	0.591	<LOD	<LOD	1.24	8.37	<LOD	25.5	0.962	1.40
GW 48	37.3	8.2	<LOD	2.27	357	0.091	1.18	0.759	134	1.61	5.16	<LOD	36.5	0.966	1.60
GW 49	36.4	5.9	<LOD	183	14.1	<LOD	0.730	<LOD	<LOD	0.911	6.36	<LOD	22.1	0.967	1.50
GW 50	27.9	12.0	<LOD	1.76	47.2	<LOD	1.75	2.18	24.5	1.64	5.58	<LOD	87.4	0.964	1.61
GW 51	27.9	20.3	<LOD	<LOD	5.73	<LOD	0.064	<LOD	2.86	2.14	1.91	<LOD	48.4	0.965	1.58
GW 52	120	4.60	<LOD	61.1	589	0.129	0.519	<LOD	<LOD	0.342	9.90	<LOD	4.72	0.963	1.45
GW 53	91.2	16.9	<LOD	0.133	8.26	<LOD	0.523	<LOD	<LOD	4.43	8.21	<LOD	50.4	0.964	1.48
GW 54	50.1	7.10	<LOD	3.18	12.0	0.699	1.36	<LOD	24.4	1.73	4.78	<LOD	91.1	1.48	1.91
GW 55	48.1	17.0	<LOD	<LOD	3.79	<LOD	0.782	<LOD	38.2	3.08	5.17	<LOD	19.7	0.965	1.51
GW 56	49.3	21.4	<LOD	11.9	9.20	0.971	0.619	<LOD	43.6	0.330	6.70	<LOD	11.7	0.962	1.59
GW 57	12.9	31.7	<LOD	<LOD	8.43	<LOD	<LOD	<LOD	<LOD	1.67	0.801	<LOD	17.6	0.961	1.65
GW 58	47.5	23.5	<LOD	<LOD	2.79	<LOD	<LOD	<LOD	5.19	0.934	2.06	<LOD	20.8	0.961	1.54
GW 59	40.8	33.1	<LOD	<LOD	7.33	<LOD	<LOD	<LOD	0.640	0.701	1.19	<LOD	7.82	0.961	1.59
GW 60	18.7	33.2	<LOD	0.663	6.03	0.081	1.02	<LOD	<LOD	2.03	1.23	<LOD	14.5	0.963	1.54

<LOD means: concentration is below limit of detection

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