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Abstract
Abstract The present study was carried out to assess the quality of drinking water produced by private pilot desalination stations designed to lower the groundwater salinity in Hail city, Kingdom of Saudi Arabia. The assessment was done by investigating the physico- chemical water characteristics and heavy metals concentrations. Representing water samples were collected from the drinking water treatment stations scattered along the seventeen districts in Hail city. Water quality characteristics include: pH, Turbidity, TDS, NO2-, NO3-, Ca2+, Mg2+, total hardness, calcium hardness and magnesium hardness as well as the concentrations of the heavy metals: Fe, Mn and Pb. Water quality parameters were compared to the Saudi and Gulf standards for unbottled drinking water. The obtained results revealed that most of the studied parameters fall within the national and regional standards. However, some treatment stations showed high concentrations of the heavy metals above the permissible levels, which cause undesirable health and aesthetic effects, and make them unfit for human consumption. Accordingly, there is an urgent need for the
continuous monitoring of these water desalination plants and implementation of all the environmental health regulations and conditions by the responsible local governmental authorities.

1. Introduction [•]

Groundwater is the main source of drinking water in the Kingdom of Saudi Arabia; KSA (Mohamed, *et al.*, 2015, Toumi, *et al.*, 2013 and AI-Abdula'aly, 1997). In Hail region of KSA, groundwater that is extracted from the wells is the source of water for the private unbottled drinking water treatment stations (pilot desalination stations) scattered along the capital of the region; Hail city. These water treatment stations reduce drinking water salinity in order to make the water suitable for drinking.

Hail City is one of the promising regions in KSA, through its evolving agricultural, commercial, economic and educational activities in addition to the historical tourism activities. Nowadays, it is considered as the northern capital of the kingdom. Accordingly, many work opportunities are available in both of the different governmental and private sectors. Therefore, Hail became an attracting city for work and living. Hence, there is an increasing demand for a cheap drinking water in the city to meet the inhabitants needs. The main sources for drinking water in Hail city -like most of the cities in Saudi Arabia- are the bottled natural drinking water, in addition to the unbottled drinking water produced by the private drinking water treatment stations. This unbottled drinking water is cheaper than the bottled water, and in turn it is an attracting for many residents of the city.

The private drinking water treatment stations that produce the unbottled drinking water, are scattered along Hail city. They receive water by tankers from productive water wells north of Hail city, and apply some chemical and physical treatment processes including the reverse osmosis technique to reduce the water salinity to the acceptable level and to remove suspended particles and microorganisms from water.

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Because of the gradual increase of the number of these private drinking water treatment stations in the city, there is a great necessity for a continuous monitoring and assessment of the quality of drinking water produced via these water treatment stations in order to protect the human health in the region.

In the year of 2005, the General Directorate of Environmental Health, Ministry of Municipal and Rural Affairs, KSA, has issued the list for the requirements and conditions that should be available at the stations reducing drinking water salinity (GDEH, 2005). The quality of the unbottled drinking water produced from these stations should comply with this list of requirements, in addition to the Saudi Standards cited by the Saudi Arabian Standards Organization (SASO) (2000), and Gulf Standards (GS) (2000) for unbottled drinking water. Few studies were carried out to assess the quality of water of the wells in Hail region; the sources of the unbottled drinking water of Hail city, e.g., Al-Turki (2009); Sulieman et al. (2015); Alshammari et al. (2016) and Abdel-Satar et al. (2017). Another study has investigated the quality of the tap water collected from the newly established water project of Hail; the governmental drinking water treatment station (Mohamed, et al., 2015). All these previous studies indicated that the quality of water in some wells of Hail region is not good enough, to be used as a suitable source for the drinking water in Hail city. In addition, Sulieman et al. (2015) carried out an assessment of water quality upon three private desalination stations in Hail and observed that results were within the allowable levels for drinking water. However, no comprehensive study was, yet performed at a large spatial scale in the region. Hence, the present study aims to give an insight to the quality of unbottled drinking water at Hail city scale.

Materials and Methods

The Study Area

Hail city was chosen as the study area as no source of freshwater except the water from underground. The region of Hail is located in the northern part of Saudi Arabia with an area of about (120,000 km²), between longitudes 39°26'52"E and 44°22'42"E and latitudes 25°16'34"N and 28°53'16"N (Figure 1). It has a typical desert climate, with cool winters and hot summers (Abdel-Satar, et al., 2017). Air temperature ranges between about 10°C in winter to more than 32°C in summer. Hail region is bordered from the north by an extensive sand dune field known as Al-Nafud Sand Sea. The city of Hail occurs at the foot of Aja Mountain which attains a height of 1480 m above sea level, making the urban neighborhoods close to the highland frequently exposed to torrential flooding, particularly in the fall and spring semesters (Hereher et al., 2012). The valleys of the Aja Mountain are significant sources to recharge the groundwater aquifer. Hail city is considered as the fifth city in regard to its area in KSA (Sulieman, et al., 2015). There are tremendous development activities in the city and its vicinity. Beside urbanization, agricultural sector also contributes to the fast growing development activities, depending upon the reserves of groundwater in Saq Formation north of Hail which has water salinity ranging from 300 to 1000 ppm (Sharaf and Hussein 1996).

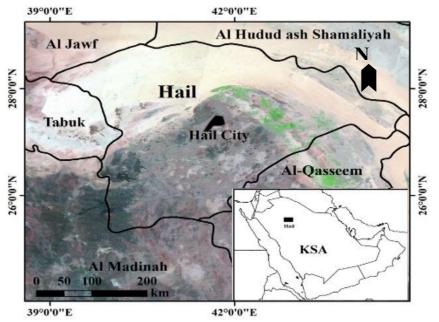


Figure (1): Map of the area under study (after Hereher *et al.*, 2012)

Sampling and analysis

Seventeen private unbottled drinking water treatment stations (pilot desalination stations "DS") that reduce the salinity of drinking water, were selected as study sites in Hail city. These sites are scattered along the seventeen districts in the city (Table 1). A grab drinking water sample was collected form each site in Spring 2017 for analysis. The Physico-chemical characteristics; in terms of pH, Turbidity, Total Dissolved Solids (TDS), Nitrites (NO₂⁻), Nitrates (NO₃⁻), Calcium (Ca²⁺), Magnesium (Mg²⁺), Total Hardness (T.H), Calcium Hardness (Ca.H) and Magnesium Hardness (Mg.H) were analysed. Moreover, some heavy metals concentrations (Fe, Mn and Pb) were selected for investigation. Water samples were collected in high density polyethylene bottles from the outlet of the final reservoir of the DS. The water was pumping out from the outlet of the final reservoir to the sampling bottles through a long hose, as it works always in these DS when they pump out the treated water to the consumers. The collected samples were kept cool in an ice box until transported to the chemical laboratory of the Faculty of Public Health at Hail University. Some parameters were measured immediately *in Situ*, such as the pH, Turbidity and TDS in water. The other parameters were measured in the laboratory of the Faculty of Public Health. At the laboratory, the samples were stored at 4 °C and the analyses were conducted within the same day of sample collection.

 Table (1): Study sites of the collected drinking water samples

Site	Study Sites									
Number	Station Name	Street Name	District Name Alnokrah							
1	Ynabeea Alshfa	Road Alnokrah								
2	Abar Alshmal	Road Alamer Souod Bn Abdulmhsen	Alsbhan							
3	Alshalal	Road 30	Ammar							
4	Alwaseta	Road Alamer Sultan Bn Abdulaziz	Alwaseta							
5	Sbabh	Road Ebn Batotah	Almhattah							
6	Alshalal 2	Road Almarwh	Alazeziah							
7	Miah Thliah	Road King Khaled	Salah Aldeen							
8	Siol	Road Ebn Baz	Albadiah							
9	Alkwtthr	Road Almoslmany	Brzan							
10	Alzlal	Road Obadh bn Obidah	Altrefe							
11	Al-Nada	Road Alzeraah	Aga							
12	Namerah	Road Alkarbe	Alazezuah							
13	Alzeer	Road King Fisal	Alazezuah							
14	Miah Thliah II	Road Alamer Fisal	Sdian							
15	Alsalsbeel	Road Alamer Naif	Eeirf							
16	Sama	Road Alamer Mkrn Bn Abdulaziz	Alzbarah							
17	Shakhaleel Aga	Road Alsenaeiah	Alkhmashiah							

All physico-chemical characteristics and heavy metals were conducted according to the standard methods for water and wastewater examination (APHA, 2005) and the instruction manual of the used instruments when applicable. The pH was measured using a pH meter model 350 Jenway, UK., while turbidity was determined by TURBIDITY meter TurbiDirect 300 Lovibond, Germany. TDS was analyzed using the TDS meter model 4520 Jenway, UK. At the same time, nitrates and nitrites were analyzed using the Lovibond SpectroDirect 712000, UK, while T.H., Ca.H., Ca^{2+} , Mg.H., and Mg²⁺ were determined by the EDTA complexometric titration method. Heavy metals concentrations (Fe, Mn and Pb) were determined after preconcentration by digestion with nitric acid, followed by solvent extraction using ammonium pyrrolidine dithiocarbamate and methyl isobutyl ketone,

then estimated using atomic absorption spectrophotometry Shimadzu AA7000 (Japan).

Statistical analysis

In order to explore the significance and relationships between all the investigated drinking water quality characteristics, the correlation coefficient was identified using the IBM SPSS version 24 statistics program. Correlation coefficient is usually used to establish the relation between independent and dependent variables (Gad *et al.*, 2018). The mean values and standard deviations for the measured characteristics were also calculated using the same program.

Results and Discussion

Physico-chemical characteristics

The results of the studied drinking water characteristics for the collected samples are presented in (Table 2), whereas the correlation matrix for the studied characteristics are shown in (Table 3). The pH values for the seventeen unbottled drinking water samples ranged from 7.15 to 8.62, with a mean value of $8.02 \pm$ 0.29. All the pH values were within the Saudi and Gulf permissible limits (SASO, 2000 and GS, 2000), except for the DS no. 5, which was slightly high (8.62) and exceeding the permissible limits. For effective disinfection with chlorine, the pH should preferably be less than 8 (WHO, 1996). Other physico-chemical characteristics: Turbidity, TDS, NO₂⁻, NO₃⁻, Ca²⁺, Mg²⁺, and T.H were within the permissible levels of the unbottled drinking water. The mean value for the Turbidity of all the investigated water samples was 0.27 \pm 0.21 NTU, while it was 225.88 \pm 78.09, 0.17 \pm 0.35 and 5.47 \pm 2.78 mg/l for TDS, NO₂⁻ and NO₃⁻, respectively. Regarding the Ca²⁺, Mg²⁺, T.H, Ca.H and Mg.H; the mean values for each of them was $35.39 \pm$ $8.75, 11.38 \pm 6.93, 132.79 \pm 30.47, 85.92 \pm 21.63$ and 46.87 ± 28.54 mg/l, respectively.

Nitrate is an indicator of organic contamination and the increase in nitrogenous pollutants leads to an increase in nitrate level (Rawat, *et al.*, 2019). In the present study, the NO₃⁻ concentrations in all studied drinking water samples fall within the permissible levels. This is might indicates that there is no organic pollution in the water samples. Comparing the results of the physico-chemical characteristics in the current study with those of Sulieman *et al*, (2015) about the drinking water quality of a few private DS in Hail city, reveals coincidence of the main trend as they are mostly fall within the permissible standards for the unbottled drinking water quality.

Heavy metals

The obtained values for the heavy metals (Fe, Mn and Pb) in all study sites are shown in Table (2) and Figures (2 - 4). Concentrations of Fe were mostly within the permissible levels of the unbottled drinking water in all the studied DS, except for study sites no. 5 and no. 14, in which Fe concentration were 0.352 and 0.334 mg/l respectively, and slightly exceeding the permissible level. At the same time, Mn concentrations were recorded at some of the study sites; no. 11, 15 and 17 as 0.589, 0.514 and 0.543 mg/l respectively, slightly higher than the Saudi and Gulf standards for unbottled drinking water. Moreover, analysis of Pb in the investigated DS revealed that there was an increase in its concentration in four of the studied sites. Pb was significantly exceeding the permissible limits in the

study sites numbers 5, 6, 14 and 17, in which recorded as 0.014, 0.012, 0.018 and 0.021 mg/l respectively. These results for Pb in the studied sites coincide to some extent with the findings of Abdel-Satar et al. (2017), which showed that about 43% of water samples collected from the wells of Hail region were contained Pb levels higher than the drinking water guidelines. Moreover, the situation that the working water desalination stations in Hail city are unable to remove Pb concentrations from the treated water, conforms with the result of a previous study (Hereher, and El-Ezaby, 2012) on a water desalination station of Marsa Alam at the Red sea coast, Egypt. This desalination station was also unable to remove the high Pb concentration (0.033 mg/l) from its treated water. Hereher (2017) reported that ponded water accumulated behind Wismy Dam in the granitic Aja Mountain of Hail has acceptable levels of heavy metals except for Pb. He observed that the concentrations of Pb is 3-5 folds of the United States Environmental Protection Agency standards. As the Aja Mountain is a primary source of water to the underground aquifer, high levels of Pb could reach to the aquifer, which is the case in the study area. Lead is highly toxic element and can be amassed in the skeletal structure of human (Musa et al., 2013). Bioaccumulation of lead in the body may cause permanent damage to the central nervous system and brain, high blood pressure, hearing problems and reproductive problems in men, while slowed growth, digestive problems, headaches, joint and muscle pain may occur in women (Mkude, 2015).

Elevated levels of iron in water can cause upset in the gastrointestinal tract and can affect the taste of water by enhancing the growth of iron bacteria, which infer their energy from the oxidation of ferrous iron into ferric iron. When the iron is oxidized from ferrous to ferric state, it gives an obvious reddish-brown color to water. In addition, iron in water has the potential of staining metal and laundry pipes for reticulation (Musa et al., 2013 and WHO, 2017). When manganese levels exceed 0.1 mg/l in water supplies, it may cause an objectionable taste in beverages and stains sanitary ware and laundry. The presence of manganese in drinking water could cause the buildup of deposits within the distribution system. According to the World Health Organization, the health-based permissible level for Mn in drinking water is 0.4 mg/l (WHO, 2017).

Correlation significance

The correlation matrix between the investigated unbottled drinking water quality characteristics (Table 3) revealed that Pb showed high significant correlation with NO₂⁻, NO₃⁻ and Fe, while it was correlated medially with pH. At the same time, T.H was highly significant correlated with Mg²⁺, likewise, NO₃⁻ showed high significant correlation with NO_2^- . In addition, Mn was medially correlated with pH, Ca^{2+} and T.H. There was also significant medium correlation between T.H and TDS. The mean values with standard deviations for the all investigated characteristics were shown in (Table 2).

Correlation significance

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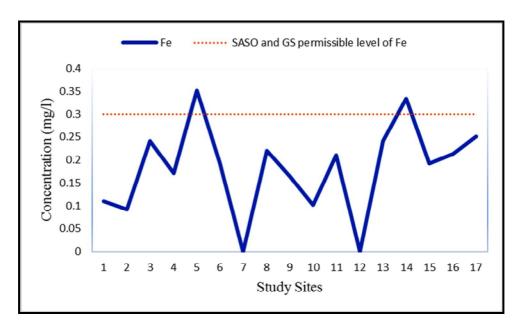
Conclusion

This study aimed to assess the quality of unbottled drinking water produced by the private desalination stations that reduce the salinity of drinking water in Hail city, KSA. The obtained results revealed that most of the measured physico-chemical drinking water characteristics were within the permissible levels of the national (SASO) and regional (GS) standards for unbottled drinking water. However, it was obvious that the values of some water quality characteristics; pH, iron, manganese and lead in some of the studied DS were exceeding the standards of unbottled drinking water. As a consequence, the unbottled drinking water produced by these uncontrolled treatment stations is unsuitable for drinking purposes. Therefore, there is an urgent need for adopting a feasible routinely monitoring system for these private DS and to the productive wells from which they abstract the raw water as well. High levels of heavy metals in the analyzed drinking water samples of the current investigation should pay attention to the officials of the Environmental Health Department, the Municipality of Hail city and the branch of the Ministry of Health in the city, to deal quickly with this environmental and health issues. The Health authority in conjunction with the Environmental Health Department in Hail city should ensure the implementation of all the environmental health regulations and conditions, in addition to applying all the technical requirements, which are relevant to the production of safe unbottled drinking water from these private drinking water treatment establishments.

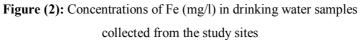
Site Number	рН	Turbidity <i>(NTU)</i>	TDS (mg/l)	NO2 ⁻ (<i>mg/l</i>)	NO3 ⁻ (<i>mg/l</i>)	Ca ²⁺ (<i>mg/l</i>)	Mg ²⁺ (<i>mg/l</i>)	Т.Н (<i>mg/l</i>)	Ca.H <i>(mg/l)</i>	Mg.H (<i>mg/l</i>)	Fe (<i>mg/l</i>)	Mn (<i>mg/l</i>)	Pb (<i>mg/l</i>)
1	7.15	0.19	168	0.15	3.7	24.1	9.1	97.4	59.8	37.6	0.110	ND	ND
2	7.76	0.14	378	0.19	4.3	25.3	2.4	99.1	89.2	9.9	0.092	ND	ND
3	8.01	0.79	386	ND	5.7	35.1	31.4	216.6	87.3	129.3	0.241	0.272	0.003
4	7.85	0.44	176	ND	3.9	33.3	11.5	130.4	83.0	47.4	0.172	0.353	ND
5	8.62	0.14	202	ND	4.1	29.3	16.4	140.6	73.0	67.6	0.352	0.387	0.014
6	8.07	0.30	217	0.16	4.9	35.9	10.0	130.8	89.6	41.2	0.192	0.211	0.012
7	7.98	0.15	135	ND	5.8	29.0	4.9	93.3	73.2	20.1	ND	0.088	ND
8	8.13	0.06	102	0.15	4.9	21.3	12.2	103.5	53.1	50.4	0.221	0.082	0.004
9	7.99	0.14	227	ND	3.6	41.3	9.7	143.2	103.1	40.1	0.164	ND	ND
10	7.97	0.15	225	0.19	5.1	37.2	10.8	137.1	92.5	44.6	0.102	0.048	ND
11	8.14	0.32	226	ND	4.2	58.5	1.9	146.0	138.0	8.0	0.211	0.589	0.005
12	8.18	0.16	227	ND	4.9	43.9	8.3	143.5	109.5	34.0	ND	0.247	ND
13	7.79	0.43	170	0.15	3.8	38.5	5.5	116.2	93.7	22.5	0.242	ND	ND
14	8.24	0.73	226	0.21	8.6	41.3	13.6	102.9	47.1	55.8	0.334	0.270	0.018
15	8.10	0.12	189	ND	4.0	37.2	11.5	140.2	92.7	47.5	0.192	0.514	ND
16	8.13	0.19	242	0.16	6.4	32.0	18.7	156.6	79.7	76.9	0.213	0.334	0.003
17	8.17	0.17	344	1.48	15.1	38.5	15.5	160.1	96.2	63.9	0.251	0.543	0.021
Mean	8.02	0.27	225.88	0.17 ±	5.47 ±	35.39	11.38	132.79	85.92	46.87	0.182	0.232	0.005
	$\stackrel{\pm}{0.29}$	± 0.21	$^{\pm}_{78.09}$	0.17 ± 0.35	2.78	± 8.75	± 6.93	± 30.47	± 21.63	± 28.54	$\overset{\pm}{0.098}$	± 0.196	$_{0.007}^{\pm}$
(SASO, 2000) and (GS, 2000)	6.5- 8.5	5	1000	3	50	200	150	500	-	-	0.3	0.5	0.01

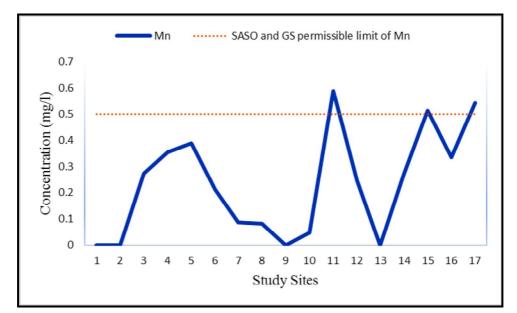
Table (2): Results of the analyzed physical-chemical characteristics of the investigated drinking water samples

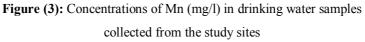
Note: ND: Not Detected



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	pН	Turbidity	TDS	NO ₂ ⁻	NO ₃ -	Ca ²⁺	Mg ²⁺	Т.Н	Ca.H	Mg.H	Fe	Mn	Pb
pН	1												
Turbidity	0.02	1											
TDS	0.07	0.31	1										
NO ₂ -	0.07	-0.11	0.39	1									
NO ₃ -	0.28	0.11	0.41	0.91**	1								
Ca^{r_+}	0.30	0.28	0.16	0.01	0.10	1							
Mg^{r_+}	0.28	0.46	0.38	0.12	0.29	-0.17	1						
T.H	0.34	0.35	0.57^{*}	0.12	0.21	0.37	0.73**	1					
Ca.H	0.11	-0.12	0.31	0.01	-0.09	0.75**	-0.29	0.44	1				
Mg.H	0.28	0.46	0.38	0.12	0.29	-0.17	1.00**	0.73**	-0.29	1			
Fe	0.46	0.42	0.10	0.21	0.26	0.10	0.47	0.27	-0.23	0.47	1		
Mn	0.52*	0.13	0.19	0.28	0.40	0.50^{*}	0.25	0.49*	0.35	0.25	0.42	1	
Pb	0.55*	0.22	0.24	0.63**	0.73**	0.14	0.28	0.12	-0.21	0.28	0.66**	0.48	1

Table (3): Correlation matrix between the investigated drinking water quality characteristics

* Correlation is significant at the 0.05 level; ** Correlation is significant at the 0.01 level.

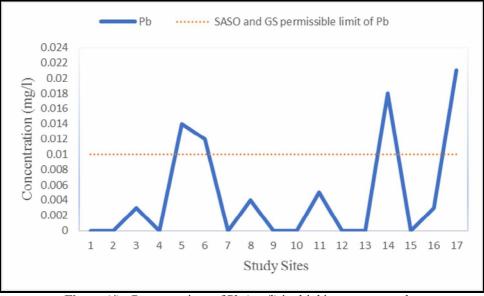


Figure (4): Concentrations of Pb (mg/l) in drinking water samples collected from the study sites

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