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Research Article

Classification and Evaluation of Commercial Bottled Drinking Waters in Saudi Arabia

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Abstract: This study reports an evaluation on the quality of 54 brands of bottled drinking waters currently consumed in Saudi Arabia. The relationships among eight selected major chemical ion variables (calcium, magnesium, sodium, potassium, chloride, sulfate, bicarbonate and nitrate) were examined by correlation analysis, principal component analysis and hierarchical cluster analysis. Principal component analysis identified three factors, which are responsible for the data structure explaining ~64% of the total variance of the data set and allowed to group the selected parameters according to common features. Hierarchical cluster analysis classified the evaluated water brands into different groups based on the similarity of water quality characteristics. The results demonstrated that the water brands have a diverse character reflected by their chemical compositions and are dominated by Na-Ca-HCO_3-Cl type water. Total hardness values classified most of the studied brands into soft to moderately hard water. Generally, the physical and chemical constituents lie within the acceptable boundaries established by Saudi Arabian Standards Organization, International Bottled Water Association, Food and Drug Administration and World Health Organization for drinking water.

Keywords: Bottled water, cluster analysis, principal components, Saudi Arabia, water quality

INTRODUCTION

Mineral content of bottled water is one of the most important markers for water quality. Some minerals are of importance in our daily lives, which play a significant role in the nutrition of our bodies (Saleh *et al.*, 2008). These minerals are divided into two classes: those required in our diet in excess of 50 mg/day are designated as macro elements and those required in < than 50 mg/day are called trace elements. Epidemiological studies reported a strong correlation between various human diseases and the presence of trace elements in drinking water (Krachler and Shotyk, 2009).

To assess the quality of drinking bottled water, various studies have been conducted in Saudi Arabia during the past two decades (Alam and Sadiq, 1988; Alabdula'aly and Khan, 1995, 1999; Khan and Chohan, 2010; Aldrees and Al-Manea, 2010). Metal concentrations assessment in nine bottled water brands marketed in Saudi Arabia was performed by Alam and Sadiq (1988). As per their results the concentrations of calcium and sodium in two brands were higher than the values printed on their labels. Following this, Alabdula'aly and Khan (1995) evaluated the microbiological quality of fourteen local and six imported brands in Saudi Arabia for total coliform and heterotrophic plate counts. Their study could not detected coliform in any of the water samples. Another study of Alabdula'aly and Khan (1999) revealed that the levels of total dissolved solids, calcium, magnesium, sodium, potassium, nitrates, chloride, sulfate in fourteen domestic and seven imported brands of bottled water in Saudi Arabia remained within the permissible limits of local and international standards. Twenty one different brands of locally produced bottled water in Riyadh (Saudi Arabia) were investigated by Khan and Chohan (2010), which revealed a concentration of higher levels of fluoride than the labeled values (ranged between 0.32 and 1.1 mg/L with a mean value of 0.86 mg/L). According to Aldrees and Al-Manea (2010), the fluoride content in the twelve Riyadh based water bottles ranged from 0.5 to 0.83 mg/L with a mean value of 0.79 mg/L. Bottled drinking waters consumed in Riyadh contain differing concentration of fluoride, but within a safe range.

Demand for bottled water in Saudi Arabia and other countries of the world registered a significant increase due to the growing population and concern about contaminants in natural water supplies (Ikem *et al.*, 2002; Versari *et al*., 2002; Ahiropoulos, 2006; Güler, 2007; Güler and Alpaslan, 2009; Birke *et al.*, 2010; Frengstad *et al.*, 2010; Kermanshahi *et al*., 2010; Dinelli *et al*., 2010; Bityukova and Petersell, 2010; Cidu *et al*., 2011). Due to an increasing demand in Saudi Arabia, several new brands have been introduced in the market. The water quality of these new brands have been not assessed or investigated to the best of our knowledge. The purpose of this study is to investigate the physico-chemical characteristics of some of the most widely distributed domestic brands of bottled drinking waters sold in Saudi Arabia and to compare them with parameters printed on their labels. For this purpose, a total of 54 domestic and imported brands were characterized using multivariate methods including Correlation Analysis (CA), Principal Components Analysis (PCA) and Hierarchical Cluster Analysis (HCA). In addition the obtained chemical parameters were compared with standards adopted for drinking water in Saudi Arabian and internationally. Results of this study may be useful for improving the current legislation on bottled waters and also for guiding the consumers in their choices for suitable brands.

MATERIALS AND METHODS

Water samples collection: A total of 52 brands of domestically produced bottled waters and two imported brands from Kuwait (all non-carbonated), consisting both the groundwater and the processed water, were purchased randomly from local supermarkets and independent food stores throughout Saudi Arabia (Fig. 1). The water samples were collected between March and June 2011. As indicated on their labels, all the sampled bottles were valid for one year from the production date as per the Saudi Ministry of Health certification. All the water samples were stored in separate Polyethylene Terephthalate (PET) bags with plastic screw caps. The holding capacities of bottled water containers varied between 0.25 and 20 L. Most of the water brands contain the following parameters: pH, Total Dissolved Solids (TDS), Total Hardness (TH), Calcium (Ca), Magnesium (Mg), Sodium (Na), Potassium (K), Bicarbonate (HCO_3), Sulfate (SO_4), Nitrate (NO_3), Chloride (Cl), Fluoride (F) and Iron (Fe). Analysis and determinations of the physico-chemical parameters were carried out by the manufactures. Regular chemical analysis of this bottled water was carried out by each company on a daily basis.

Multivariate analysis/Correlation Analysis (CA): In the current study, "Pearson r correlation" was used to evaluate the linear relationships between various pairs of variables, with statistical significance set at $p<0.01$ and $p<0.05$. The value of correlation coefficient ranges between −1.0 and +1.0. The earlier value (-1.0) represents a perfect inverse relationship between the two variables, whereas the later one (+1.0) occurs when the two variables react in exactly the same way as their values change. A correlation coefficient of zero suggests that the two variables are independent of each other.

Multivariate analysis/Principal Components Analysis (PCA): PCA is used to reduce a large number of variable parameters (identified in water samples) to a small number of principal components (Versari *et al*., 2002; Brereton, 2003; Astel *et al*., 2007, 2008; Güler, 2007; Simeonova and Simeonov, 2007; Mencio and Mas-Pla, 2008; Kermanshahi *et al*., 2010; Dinelli *et al*., 2010). More concisely, PCA has been used linearly combines two or more correlated variables into one. Varimax normalized rotation was applied to the principal components in order to reduce the contribution of significantly minor variables, leaving for consideration only factors with eigen values greater than one.

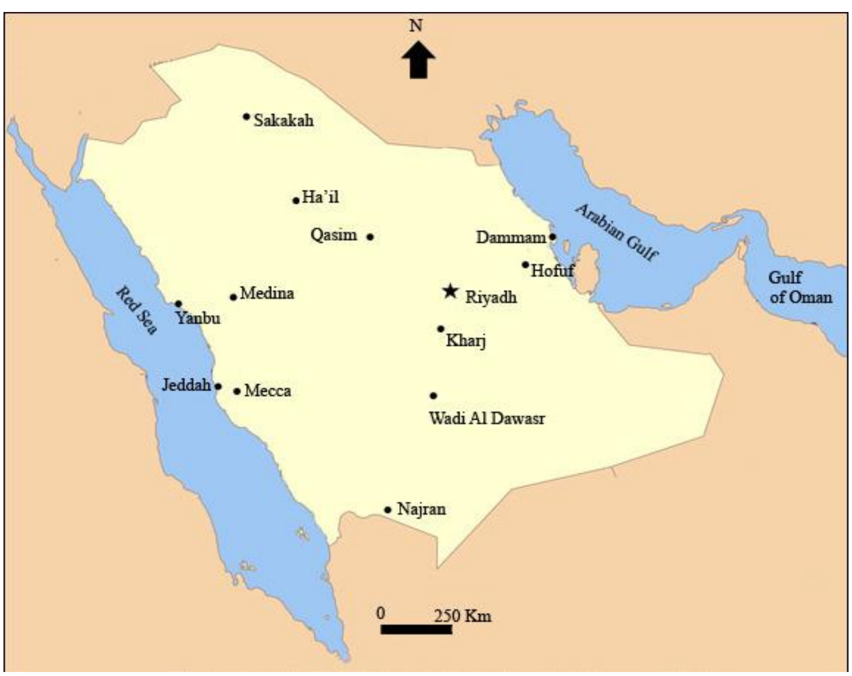

Fig. 1: Map of Saudi Arabia showing the location of bottled water production

Multivariate analysis/Hierarchical Cluster Analysis (HCA): The HCA (Meng and Maynard, 2001; Güler *et al*., 2002; Güler, 2007; Simeonova and Simeonov, 2007; Astel *et al*., 2008; Kermanshahi *et al*., 2010; Dinelli *et al*., 2010) was used to determine if the selected brands of water can be grouped into statistically distinct groups (clusters). These water brands were classified according to their major ion composition, for which the Ward's method was used as amalgamation rule to obtain the hierarchical associations. The obtained data were standardized (z-scores) and the Euclidean distance was used as similarity measurement. Classification results of the HCA are generally presented in a graphical form called "dendogram". The statistical analyses of data were performed using SPSS 13.0.

RESULTS AND DISCUSSION

Chemical characteristics of bottled waters: The physico-chemical properties for 54 brands of bottled water in Saudi Arabia are summarized in Table 1. Comparison of these values with those set by the Saudi Arabian Standards Organization (SASO, 2009),

Table 1: Major ions concentration and physical properties of bottled waters in Saudi Arabia

Brand code	Brand name	Capacity (Liter)	pH	TDS	Ca	Mg	Na	mg/L (ppm) K	Fe	HCO_3	SO_4	NO_3	Cl	F	BrO_3
1	Hayat	0.33	7.2	125	10.0	3.0	20.0	1.30	0.01	37.0	18.0	6.00	25.0	0.85	-
2	Tania	19	7.2	120	14.4	3.0	12.2	1.50	0.00	24.0	28.0	2.00	17.5	0.90	-
3	Farah	19	7.2	116	25.0	11.0	25.0	1.00	0.01	25.0	22.0	7.00	25.0	1.00	-
4	Al-Loulouah	19	7.1	125	10.0	2.4	18.0	1.40	-	30.0	11.8	3.10	25.0	1.00	-
5	Hana	0.60	7.2	127	8.0	3.0	18.0	2.00	-	28.0	36.0	25.00	32.0	0.85	-
6	Aquafina	0.60	7.0	110	<5	13.0	16.0	1.00	0.01	1.3	51.0	<0.10	27.5	1.00	-
7	Fayha	0.60	7.0	110	15.0	4.0	13.0	0.90	0.02	12.0	50.0	4.00	14.0	0.90	-
8	Safa	0.60	7.0-7.6	100 - 155	19.0	3.0	19.0	1.80	0.00	39.0	27.0	2.80	33.0	1.00	<0.01
9	Mozn	0.30	7.0-7.6	160 - 175	17.0	7.0	20.0	2.50	0.00	80.0	12.0	2.00	27.0	1.00	-
10	Pure Life	0.60	7.1	235	36.0	4.7	18.0	0.20	0.02	42.0	22.0	0.50	68.0	0.00	<0.01
11	Zulal	0.33	7.2	133	21.0	4.5	20.0	1.20	0.01	37.5	32.0	7.10	20.0	0.80	-
12	Al-Qassim	0.60	7.1	125	8.4	1.0	22.4	0.50	-	7.0	21.0	2.00	32.0	0.95	-
13	Dala	0.60	7.0-7.6	120-140	9.5	3.5	19.0	1.70	0.00	24.0	22.0	1.20	26.0	1.00	-
14	Arwa	0.50	6.7	120	0.3	22.0	1.4	0.40	<0.10	6.2	88.0	<0.10	<1	<1	-
15	Yana bea Alwadi	2	7.0-7.6	120-140	9.5	3.5	19.0	1.70	0.00	24.0	22.0	1.20	26.0	1.00	-
16	Faifa Mountain	0.60	7.0-7.8	100-150	18.0	6.0	22.0	2.00	-	70.0	15.0	5.00	25.0	1.00	-
17	Dome	19	7.2	110	14.0	4.0	13.0	1.20	0.00	28.0	29.0	11.00	15.0	0.91	-
18	Al Manhal	19	7.0	110	16.5	2.4	12.0	0.10	<0.02	30.0	13.0	<0.05	34.0	0.90	<0.01
19	Hada	0.33	7.2	109	13.0	4.0	20.0	0.80	0.00	30.0	20.0	5.00	30.0	0.80	-
20	Nova	0.33	7.0	120	10.0	4.5	16.8	1.10	-	20.0	35.0	3.10	17.0	0.80	-
21	1	0.33	7.2	127	8.0	3.0	18.0	2.00	-	28.0	36.0	2.50	32.0	0.85	-
22	Shallal Water	15	7.0	110	16.7	2.0	13.3	0.20	0.01	22.7	22.0	0.00	26.0	0.95	-
23	Safia	19	7.5	111	16.7	2.0	13.3	0.00	<0.01	22.7	4.0	6.00	34.6	0.80	-
24	Rafan	15	7.2	120	15.0	5.0	12.0	0.20	0.01	26.0	30.0	2.00	18.0	0.90	-
25	Al Ain	19	7.3	115	14.0	25.0	19.0	0.80	0.01	42.0	15.0	6.50	21.5	0.80	-
26	Haley	0.33	7.3	110	8.8	2.4	21.0	1.50	0.01	30.0	23.0	1.40	24.0	0.90	-
27	Aloyoun	0.60	7.0	110	15.0	5.0	19.0	0.20	0.02	50.0	50.0	0.10	15.0	0.80	-
28	Maeen	0.60	7.2	135	25.0	15.0	18.5	1.30	0.01	37.0	30.0	3.50	20.0	0.90	-
29	Mawared	0.33	7.2	120	14.4	3.0	12.3	1.50	0.00	24.0	28.0	2.00	17.5	0.90	<0.01
30	Hilwa	0.60	7.4	210	28.5	11.9	23.7	13.40	0.00	120.0	47.4	0.00	32.0	0.80	-
31	Honey	0.50	7.3	110	8.8	2.4	21.0	1.50	0.01	30.0	23.0	1.40	24.0	0.90	-
32	Tamimi Health Water	0.33	7.2	123	21.2	4.5	20.0	1.20	0.01	37.5	32.0	7.10	20.0	0.80	-
33	Nabah Alhada	19	7.2	110	5.0	19.2	14.5	0.80	0.02	50.0	17.0	7.00	15.0	0.80	-
34	ABC	0.33	7.2	105	15	10	<10	<0.10	-	26.0	0.0	<0.10	<56	-	-
35	Cloud Water	0.25	7.7	120	8	2.91	23.2	1.60	0.01	23.0	21.0	2.00	22.0	0.80	-
36	Hania	5	7.3	105	14	2.0	14	0.25	0.01	34.0	8.0	3.00	24.0	1.10	-
37	Al-Rai	19	7.2	110	14.5	5.0	19.2	0.84	0.00	50.0	17.0	7.00	15.0	0.80	-
38	Springs	19	7.0	110	15.0	3.0	17	0.70	0.03	40.0	12.0	1.00	30.0	0.85	<0.01
39	Yanabi Hail	15	7.3	120	12.0	2.7	21	1.90	0.01	28.8	18.0	5.50	16.0	0.90	-
40	Juda	0.33	7.2	105	15.0	10.0	<10	<0.10	-	26.0	0.0	<0.10	<56	-	-
41	Najran	0.60	7.4	120	19.0	3.5	18	1.50	-	33.5	27.0	3.20	13.5	0.80	-
42	Sahtain	0.65	7.0	110	6.0	1.0	20	1	0	13.0	15.0	12.00	30.0	0.75	-
43	Oam	5	7.0	120-150	14.4	3.4	18.5	1.20	0.01	38.0	37.0	1.90	12.8	0.83	-
44	Sahatak	0.25	7.4	120	40.0	12.0	20	2	0.10	55.0	20.0	4.00	20.0	0.85	-
45	Naqa Alshallal	2	7.3	125	14.0	2.5	19	0.80	0.01	42.0	15.0	6.50	21.5	0.80	-
46	Al Ryan	15	7.2	110	15.0	5.0	12	0.20	0.02	50.0	50.0	0.10	15.0	0.70	-
47	Shamous water	16	7.2	120	14.4	3.0	12.3	1.50	0	24.0	28.0	2.00	17.5	0.90	-
48	Al Salama	19	7.2	110	20.0	0.01	19	3.50	0.01	35.0	25.0	7.10	28.0	0.70	-
49	Sahat Afnan	0.33	6.8-7.4	105-120	8-12	1.4-3.1	25-35	0.80-1.20	-	15-30	20-36	3-4.50	25-45	0.80-1.20	-
50	Donia	20	7.2	100-120	6.7	1.6	19.5	0.20	-	7.3	27.3	22.00	20.8	0.60	-
51	Alwadi	0.65	7.5	116	2.4	0.5	24.6	0.80	0.02	40.0	12.0	5.00	30.0	0.75	-

Table 1: Continue

52	Al Ghadeer	0.50	7.1	110	18.0	3.0	14	0.20	0.02	20.0	14.0	0.05	35.0	0.90	<0.01
53	Al Jazeera	0.33	7.3	100	11	4	20	1.60	0	17	2	1	45	0.80	<0.02
54	AlShifa	1.50	7.0	110	2	0.9	35	2	-	30	6	3.55	30	0.95	<0.01

Table 2: Quality of bottled drinking water in Saudi Arabia compared to the local and international standards

Parameter	Water brands	SASO (2009)	IBWA (2004)	FDA (2002)	WHO (2008)
pH	7-8	6.50-8.50	6.50-8.50	-	6.5-8.5
TDS (mg/L)	100-253	100-500	500	500	1000
Ca (mg/L)	0.30-40	200	-	-	100
Mg (mg/L)	0.01-25	150	-	-	50
Na (mg/L)	1.40-35	100	-	-	200
K (mg/L)	0-13.40	-	-	-	12
HCO_3 (mg/L)	1.30-120	-	-	-	125-350
SO_4 (mg/L)	0-88	150	250	250	250
NO_3 (mg/L)	0-25	50	44	44	50
Cl (mg/L)	<1-68	150	250	250	250
TH (mg/L)	15-110	200	-	-	500
F (mg/L)	0-1.20	0.8-1.50	0.80-1.70	0.80-2.40	1.5
BrO_3 (mg/L)	<0.01- <0.02	0.01	0.01	0.01	-
Fe (mg/L)	0-0.03	0.30	0.30	0.30	0.3

SASO: Saudi Arabian Standards Organization; IBWA: International Bottled Water Association; FDA: Food and Drug Administration; WHO: World Health Organization

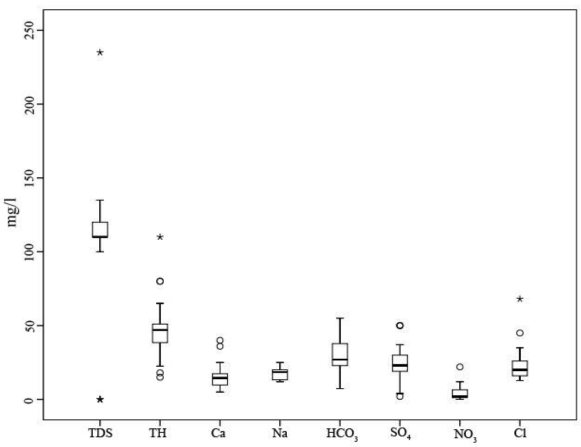

Fig. 2: Box-plot showing ion concentrations in the bottled water samples collected from the study area. Each box includes the 25th and 75th percentiles with the median displayed as a thick line; bottom and upper whiskers respective show the smallest and the largest values within the fences and the circles indicate the extreme values (outliers)

International Bottled Water Association (IBWA, 2004), Food and Drug Administration (FDA, 2002) and the World Health Organization (WHO, 2008) are also shown in Table 2. Major ions in these brands demonstrated wide variations in composition (Fig. 2), which could be attributed to natural environment from which the water is taken (geological setting, climate, topography, etc.), source water composition and type of treatments applied during their production. Additional changes in the water chemistry may also occur during storage and transportation, especially when bottles become exposed to direct sunlight (Güler *et al*., 2002).

The pH value for majority water samples range from 7 to 8 (Table 1), indicating slightly alkaline nature of the studied water. The pH variations in the studied brands are related to HCO_3 concentration, which is the most abundant ion. Recommended pH values for drinking water according to local and international standards are 6.5 to 8.5 (Table 2). Slightly alkaline water is preferable as heavy metals are removed by carbonate or bicarbonate precipitates (Ahipathy and Puttaiah, 2006). The highest TDS value (235 mg/L) is observed in Pure Life brand (Table 1). Contents of TDS in water vary significantly in different geological horizons due to the difference in solubilities of minerals. By the way, an elevated TDS concentration is not considered as a health hazard.

The highest HCO_3 concentration (120 mg/L) is found in Hilwa brand, while the lowest (1.3 mg/L) is recorded in Aquafina brand. High HCO_3 contents in the water are ascribed to chemical weathering of limestone and dolomite. Cl is the second most abundant anion and its concentration in the studied brands ranged between <1 and 68 mg/L. No sample among the studied brands has Cl levels that exceed the standard guideline recommendations. According to Zoeteman (1980), Cl levels in the excess of 250 mg/L can give rise to detectable taste in water, but the threshold depends on the associated cations. Taste thresholds for NaCl and $CaCl_2$ in water are in the range of 200-300 mg/L. Consumption of drinking water containing some Cl is not harmful for health but high amounts of it can produce a salty taste.

The SO_4 concentrations in all the water samples are within the range of Saudi and international standards for drinking water. This sulfate ion is generally harmless, except its effect on taste. The major physiological effects resulting from the ingestion of large quantities of sulfate are catharsis, dehydration and gastrointestinal irritation.

Concentrations of NO_3 in the studies water bottles vary from 0 to 25 mg/L with an average value of 4.8 mg/L. Concentrations of this nitrate ion in the bottled water samples are below the Saudi Arabian and international recommended values for drinking water. The primary health concern regarding NO_3 is the formation of methemoglobinemia, a so-called ‘blue-baby syndrome’. NO_3 can change to NO_2 in the stomach of infants, which can then oxidize hemoglobin to methemoglobin, making it difficult to transport oxygen around the body (Greer and Shannon, 2005; Sadeq *et al*., 2008). In Italy, a limit of 10 mg/L NO_3 has been recommended for the water destined to infants (Cidu *et al*., 2011).

F is an essential element for healthy teeth and is thus added to the drinking water in some countries to avoid caries. F concentrations in the studied water samples vary between 0 and 1.2 mg/L with an average value of 0.84 mg/L. The maximum allowable limit of F in drinking water is 1.5 mg/L according to WHO (2008). Concentrations of F>1.5 mg/L may cause damage to teeth under formation (dental fluorosis) (Hardisson *et al*., 2001). Minor concentrations of Bromide (<0.01 mg/L) are found in some of the brands.

Concentrations of Na varied from 1.4 to 35.0 mg/L with an average value of 18.4 mg/L. None of the values exceeded the maximum limit of 200 mg/L set by WHO (2008) (Table 2). Most of the water brands contain lower amounts of Na. An excess of Na>200 mg/L in drinking water may cause a salty taste or odor, as well

Table 3: Classification of bottled drinking water brands based on total hardness values

Brand code	Water type	Total hardness	Water hardness type
1	$Na-Ca-HCO_3-Cl$	37	Soft
2	$Ca-Na-SO_4-HCO_3$	40	Soft
3	$Ca-Na-HCO_3-Cl$	45	Soft
4	$Na-Ca-HCO_3-Cl$	-	-
5	$Na-Ca-SO_4-Cl$	-	-
6	-	53	Moderately hard
7	$Ca-Na-SO_4$	55	Moderately hard
8	$Ca-Na-HCO_3-Cl-SO_4$	60	Moderately hard
9	$Na-Ca-HCO_3-Cl$	-	-
10	$Ca-Na-Cl-HCO_3$	110	Hard
11	$Ca-Na-HCO_3-SO_4$	80	Moderately hard
12	$Na-Ca-Cl-SO_4$	-	-
13	$Na-Ca-Cl-HCO_3-SO_4$	36	Soft
14	-	-	-
15	$Na-Ca-Cl-HCO_3-SO_4$	36	Soft
16	$Na-Ca-HCO_3$	-	-
17	$Ca-Na-SO_4-HCO_3$	52	Moderately hard
18	-	52	Moderately hard
19	$Na-Ca-Cl-HCO_3$	-	-
20	$Na-Ca-SO_4-HCO_3$	43.54	Soft
21	$Na-Ca-SO_4-Cl-HCO_3$	-	-
22	$Ca-Na-Cl-HCO_3-SO_4$	49	Soft
23	$Ca-Na-Cl-HCO_3$	49	Soft
24	$Ca-Na-SO_4-HCO_3$	50	Moderately hard
25	$Mg-Na-HCO_3-Cl$	-	-
26	$Na-Ca-HCO_3-Cl-SO_4$	32	Soft
27	$Na-Ca-SO_4-HCO_3$	50	Moderately hard
28	$Ca-Na-Mg-HCO_3-SO_4$	40	Soft
29	$Ca-Na-SO_4-HCO_3$	40	Soft
30	$Ca-Na-HCO_3$	-	-
31	$Na-Ca-HCO_3-Cl-SO_4$	32	Soft
32	$Ca-Na-HCO_3-SO_4$	80	Moderately hard
33	$Mg-Na-HCO_3$	50	Moderately hard
34	-	-	-
35	$Na-HCO_3-Cl-SO_4$	40	Soft
36	$Na-Ca-HCO_3-Cl$	-	-
37	$Na-Ca-HCO_3$	50	Moderately hard
38	$Ca-Na-HCO_3$	45	Soft
39	$Ca-HCO_3-SO_4$	-	-
40	$Na-Ca-HCO_3-Cl$	-	-
41	$Na-Ca-HCO_3$	58	Moderately hard
42	$Ca-Na-HCO_3-SO_4$	18	Soft
43	$Na-Cl$	50	Moderately hard
44	$Na-Ca-HCO_3-SO_4$	65	Moderately hard
45	$Ca-Na-HCO_3$	-	-
46	$Na-Ca-HCO_3-Cl$	50	Moderately hard
47	$Ca-Na-HCO_3-SO_4$	40	Soft
48	$Na-Ca-HCO_3-Cl$	-	-
49	$Ca-Na-SO_4-HCO_3$	25-40	Soft
50	$Ca-Na-HCO_3-Cl-SO_4$	22.5	Soft
51	-	-	-
52	$Na-SO_4-NO_3-Cl$	57	Moderately hard
53	$Na-HCO_3-Cl$	15	Soft
54	$Ca-Na-Cl-HCO_3$	-	-

as some long-term health effects (Derry *et al*., 1990). Concentrations of Ca ranged between 0.3 to 40.0 mg/L with an average value of 14.4 mg/L. All the studied water brands have Ca levels falling within the Saudi and international standard limits. Natural water sources typically contain concentrations of up to 10 mg/L Ca. However, levels of up to 800 mg/L were found in natural water (Al-Redhaimen and Abdel-Magid, 1985). The taste threshold for the Ca is in the range from 100 to 300 mg/L, depending on the associated anion, but higher concentrations are acceptable is consumed.

Concentrations of Mg range from 0.01 to 25.0 mg/L with an average value of 4.7 mg/L. All the water brands have Mg levels well within the Saudi and International standard limits. K is the least abundant major cations, which varies between 0 to 13.4 mg/L in the studied brands. Only one brand (Hilwa) exceed the 12 mg/L level recommended by WHO (2008) standards.

The results from the current study can be used to estimate the amount of ingestion of certain elements by consumers. Adult humans between the age of 19 and 50 years require a daily intake of 1000 mg Ca, 310-420 mg Mg and 2400-3000 mg Na (Azoulay *et al*., 2001). For the bottled waters examined by this study, adult persons may take only 2.88% of their Ca Dietary Reference Intake (DRI), between 2.33 and 2.80% of their Mg DRI and between 1.22 and 1.53% of their Na DRI by drinking 2 L of bottled water per day (calculations were made using mean values). These results demonstrate that a significant portion of Saudi population are consuming inadequate levels of Ca and Mg. Epidemiological studies suggest that consumption of Mg may reduce the frequency of sudden death and Ca may help prevent osteoporosis in humans (Garzon and Eisenberg, 1998). It is suggested that consumers should chose to drink bottled water brands with an optimal mineral content, i.e., high levels of Ca and Mg and relatively low Na (below 20 mg/L) to prevent adverse health effects.

In this study, the water type is defined by all ionic constituents that contribute at least 25% to the total anionic or cationic composition of water (Table 3). The most frequently observed water type is Na-Ca-HCO_3-Cl. All the studied water brands are dominated by either Ca or Na except two brands (Al Ain and Nabah Alhada), which are dominated by Mg-Na-HCO_3. In order to perform a comparison between different bottled water types, main components (Na, K, Ca, Mg, Cl, SO_4 and HCO_3) of the 54 bottled waters are plotted on the Piper diagram (Piper, 1944). The diagram displays the relative concentrations of the major cations and anions on two separate trilinear plots, together with a central diamond plot where points from two trilinear plots are projected. As shown in Fig. 3, most of the water brands are Ca, Na, HCO_3 and Cl type water.

Classification of the water brands (Table 3) based on Total Hardness (TH) (Crittenden *et al*., 2005) shows

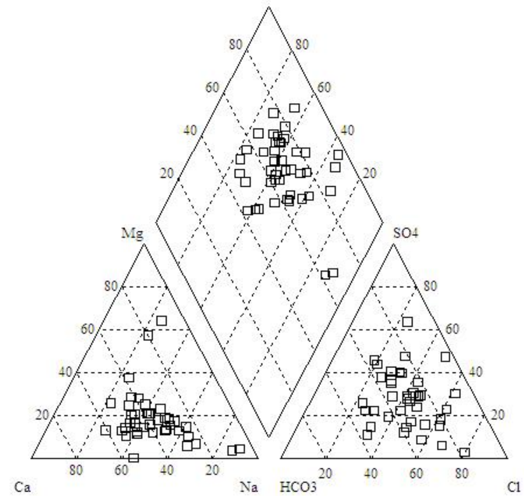

Fig. 3: Piper diagram for the bottled water brands in Saudi Arabia

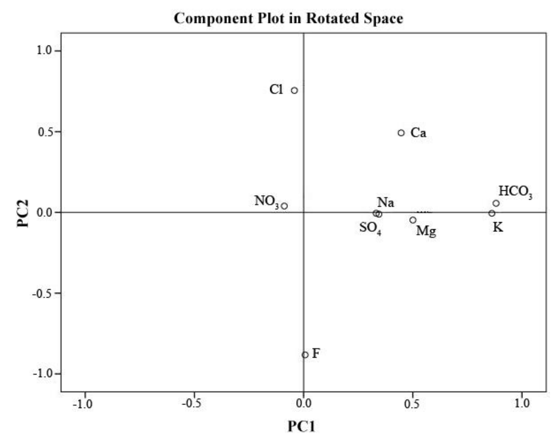

Fig. 4: Score plot of PC1 vs. PC2 illustrating the grouping of bottled water brands in 2-D PCA space

that a majority of the studied samples fall in soft to moderately hard water category. Based on this creteria the studied samples range from 15 to 110 mg/L with an average value of 47.7 mg/L (Table 3). Only one brand (Pure life) is classified as hard water. The maximum allowable limit of TH for drinking purpose is 500 mg/L (WHO, 2008), while the most desirable limit is 80-100 mg/L (Freeze and Cherry, 1979). The epidemiological studies demonstrated that water hardness may protect against certain diseases.

Multivariate analysis: Pearson's correlation coefficients among the contents of different ions are presented in Table 4. The Ca-Mg ($r = 0.33$) and Na-K ($r = 0.3$) pairs are positively correlated with each other significantly at the 95% confidence level, which may suggest a common source or a similar geochemical behavior for these metals. The Ca-HCO_3 ($r = 0.43$), Mg-HCO_3 ($r = 0.42$), K-HCO_3 ($r = 0.63$) pairs are positively correlated with each other significantly at

Table 4: Pearson's correlation coefficients between major ions in bottled drinking water brands (n = 54)

	Ca	Mg	Na	K	HCO_3	SO_4	NO_3	Cl	F
Ca	1								
Mg	0.33*	1							
Na	-0.12	-0.01	1						
K	0.24	0.18	0.3*	1					
HCO_3	0.43**	0.42**	0.20	0.68**	1				
SO_4	0.17	0.05	-0.26	0.27	0.15	1			
NO_3	-0.25	-0.04	0.05	-0.06	-0.20	0.08	1		
Cl	0.18	-0.16	0.23	0.09	0.01	-0.34*	-0.01	1	
F	-0.31*	-0.03	0.01	0.06	-0.06	-0.11	-0.04	-0.46**	1

Correlation is significant at the 0.05 level (2-tailed); Correlation is significant at the 0.01 level (2-tailed)

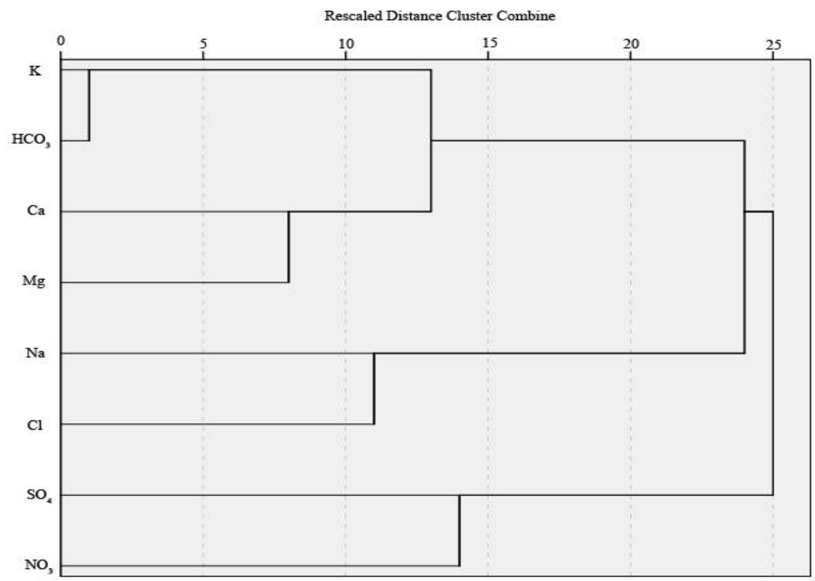

Fig. 5: Heierarchical dendrogram from the HCA for the bottled water brands

Table 5: Total variance explained and component matrix for major ions

Parameter	Component 1	Component 2	Component 3
Ca	0.65	-0.08	-0.49
Mg	0.56	-0.19	-0.07
Na	0.18	0.71	0.43
K	0.76	0.16	0.39
HCO_3	0.88	0.08	0.10
SO_4	0.30	-0.68	0.30
NO_3	-0.28	-0.04	0.65
Cl	0.03	0.72	-0.27
Explained variance	2.33	1.59	1.20
Explained variance (%)	29.10	19.92	15.01
Cumulative % of variance	29.10	49.01	64.03

99% confidence level. Negative and inverse correlations between metals indicate that these metals are derived from different sources.

PCA of the water quality variables extracts three components with eigenvalue >1.0, which account ~64% of the total variance in the dataset (Table 5). Figure 4 shows results of the PCA analysis for 54 brands of bottled water. The first Principal Component (PC1) accounted for 29% of the total variance and is characterized by high levels of HCO_3, K, Ca and Mg (with loadings 0.88, 0.76, 0.65 and 0.56, respectively). This component appears to be clearly dependent on geological composition of the substrate, being located mostly in association with carbonate rocks. Ca and HCO_3 are the major dissolved species in limestone aquifers, while the presence of Mg is attributed to either magnesian calcite or dolomite.

The second Principal Component (PC2) represents 19% of the total variance within the data and is characterized by positive loadings in Na and Cl (with loadings 0.71 and 0.73, respectively). This component represents dissolution of the evaporite minerals. The third Principal Component (PC3) is mainly related to NO_3 (with loadings 0.65), which could be due to anthropogenic inputs, mineralization and atmospheric deposition.

Hierarchical Cluster Analysis (HCA) was used for searching the natural grouping among bottled waters from different sources. The studied water brands are classified according to their major ion composition. The resulting dendrogram (Fig. 5) has three major groups based on a similarity of eight parameters. The first group characterize the water brands with Ca, Mg, HCO_3 and K. The second group represents the water brands with Na and Cl. NO_3 and SO_4 represent the third group of the water brands. The results of HCA coincide with those obtained from PCA.

CONCLUSION

Results from this study indicate that there is a wide variation in the water composition of various brands available in Saudi Arabia. The most dominant water type is Na-Ca- HCO_3-Cl. Majority of the studied brands is classified as soft to moderately hard water. The application of different multivariate statistical techniques, such as Correlation Analysis (CA), Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) provided information on the composition of water and characterized them according to their sources. PCA identified three factors, which carry ~64% of the total variance of the dataset. HCA classified the water brands into three different groups based on the similarity of water quality characteristics. The physical and chemical contents of the studied water brands are found within the acceptable limits set for drinking water by Saudi Arabian Standards Organization (SASO, 2009), International Bottled Water Association (IBWA, 2004), Food and Drug Administration, 2002) and World Health Organization (WHO, 2008).

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