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ORIGINAL ARTICLE

Physicochemical properties and the concentration of anions, major and trace elements in groundwater, treated drinking water and bottled drinking water in Najran area, KSA

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Abstract Basic information about major elements in bottled drinking water is provided on product labels. However, more information is needed about trace elements in bottled drinking water and other sources of drinking water to assess its quality and suitability for drinking. This is the first such study to be carried out in Najran city in the Kingdom of Saudi Arabia (KSA). A total of 48 water samples were collected from different sources comprising wells, stations for drinking water treatment and bottled drinking water (purchased from local supermarkets). The concentrations of 24 elements [aluminum (Al), arsenic (As), barium (Ba), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), cesium (Cs), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), molybdenum (Mo), sodium (Na), nickel (Ni), lead (Pb), rubidium (Rb), selenium (Se), strontium (Sr), titanium (Ti), vanadium (V), uranium (U) and zinc (Zn)] were determined by inductively coupled plasma-mass spectrometry (ICP-MS). Anions (chlorine (Cl^-), fluoride (F^-), sulfate (SO_4^{2-}) and nitrate (NO_3^-) were determined by ion chromatography (IC). Electrical conductivity (EC), pH, total dissolved salts (TDS) and total hardness (TH) were also measured. All parameters of treated drinking water and bottled drinking water samples did not exceed the World Health Organization (WHO) 2008, US Environmental Protection Agency (USEPA 2009), Gulf Cooperation Council Standardization Organization (GSO) 2008 and Saudi Arabian Standards Organization (SASO) 1984 recommended guidelines. It is noteworthy that groundwater samples were not used for drinking purpose. This study is important to raise public knowledge about drinking water, and to promote public health.

Keywords Groundwater · Treated drinking water · Bottled drinking water · Trace elements · Najran

Introduction

Drinking water is essential for life and is an important source of essential elements. Exposure to trace and toxic elements often occurs through drinking water. Concentrations of major and trace elements (essential and toxic) in drinking water have been investigated in several previous studies (Avino et al. 2011; Birke et al. 2010; Da Silva et al. 2000; Dinelli et al. 2012; Lee et al. 1999; Stetzenbach et al. 1994). Studies have been carried out recently on drinking water quality in Riyadh, KSA (Al-Saleh and Al-Doush 1998; Hashem 1993; Khanfar 2010; Al Nouri et al. 2014); however, only a limited range of parameters were investigated.

Worldwide, bottled water consumption has greatly increased (Datamonitor 2014), which means that there should be regular independent tests on its quality. To ensure this, worldwide standards for bottled drinking water have been set by different organizations; for example, the European Union (EU) (through the Drinking Water Directive), Food and Agriculture Organization (FAO), United States Environment Protection Agency (USEPA) and the World Health Organization (WHO) (Birke et al. 2010).

Bottled drinking water and treated drinking water are the main types of drinking water available in Najran city. Groundwater wells in the Najran valley are the main source of treated drinking water. After extraction, this

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groundwater is transported by tankers to water treatment stations across the entire city for treatment. Untreated groundwater from wells is transported directly to homes and businesses for domestic use, where it is stored in reservoirs under houses and businesses, and then is later pumped upstairs to large tanks, from where it is distributed through pipes for domestic use. Each house in the city has a complete, independent, isolated water distribution system.

The main aim of this study was to investigate the levels of major elements, non-metal elements (anions), trace elements (essential and toxic) and other parameters (physicochemical properties) in drinking water, and then to compare them with national and international guidelines. A further aim was to relate drinking water quality to public health. The findings of this research may provide further opportunities for drinking water research and treatment, which could be of benefit for public health in the KSA.

Materials and methods

Water sample collection

All samples were collected during May–July 2012. The following water samples were collected: (1) groundwater samples ($n = 11$) from different wells in the Najran valley, (2) treated drinking groundwater ($n = 13$) from commercial stations distributed throughout the city, and (3) bottled drinking water ($n = 24$) of different brands, purchased from local markets and supermarkets.

Samples were collected in polyethylene bottles that were soaked overnight in 15 % nitric acid. The soaked polyethylene containers were washed with deionized water and dried at room temperature. Afterwards, the containers were rinsed several times with the water source to ensure sufficient flushing before collection. The method of collection was similar to those reported in previous studies (Reimann et al. 2003; Barati et al. 2010; and Birke et al. 2010). All samples were stored in a refrigerator before transferred to other locations for analysis.

Analytical methods

pH and EC were measured on samples at room temperature upon arrival in Najran University, using a Lovibond sensodirect pH-200 potentiometer and a Lovibond sensodirect-200 conductometer.

Cations were measured by inductively coupled plasma-mass spectrometry (ICP-MS) at Nottingham University, Nottingham, UK. TH was calculated from Ca to Mg concentrations: Hardness in mg/L = 2.497 (Ca in mg/L) + 4.118 (Mg in mg/L) (Bryant and McPhilliamy 2002; APHA 1999). The samples were shipped by courier to Nottingham.

Anions were measured by ion chromatography (IC) at the General Directorate of Water, Ministry of Water and Electricity, Abha, KSA. TDS was also measured at the same laboratory. Samples were transferred to Abha in cold condition.

Inductively coupled plasma-mass spectrometry

Multi-element analysis of water samples was carried out using ICP-MS (X-Series^{II}; Thermo-Fisher Scientific Inc., Waltham, MA, USA) with collision cell technology with energy discrimination. A hexapole collision cell (7 % hydrogen to helium) was used to remove polyatomic interferences. Samples were introduced to the ICP-MS plasma by an autosampler (Cetac ASX-520 with 4 × 60 place sample racks), through a concentric glass venturi nebulizer (Thermo-Fisher Scientific; 1 mL/min). Details of the ICP-MS operating conditions are shown in Table 1.

Internal standards used included scandium (Sc, 100 µg/L), rhodium (Rh, 20 µg/L), germanium (Ge, 20 µg/L) and iridium (Ir, 10 µg/L), prepared with 2 % trace analysis grade HNO_3 (Fisher Scientific, UK). These were introduced to the sample stream via a T-piece. External multi-element calibration standards (Claritas-PPT grade CLMS-2 from SPEX Certi-Prep Ltd, Stanmore, Middlesex, UK) included Al, As, Ba, Cd, Co, Cr, Cs, Cu, Fe, Mn, Mo, Ni, Pb, Rb, Se, Sr, U, V and Zn, concentrations of which were in the range blank (0) up to 100 µg/L (0, 20, 40, 100 µg/L). A tailored external multi-element calibration solution

Table 1 ICP-MS Thermo-Fisher Scientific X-Series II operating conditions

Parameter	Setting
Forward power (W)	1400
Cooling gas (L/min)	13.0
Auxiliary gas (L/min)	0.70
Sampling depth (mm)	15
Add gases: 7 % H_2 in He	3.50
Nebulizer gas flow (L/min)	0.79
Torch—horizontal setting	80
Torch—vertical setting	356
DA (V)	−29.8
Main run	Peak jumping
Sweeps	120
Dwell time (ms)	10000
Channels per mass	1
Acquisition duration	51998
Channel spacing	0.02

Table 2 The LOD, LOQ of the 24 elements and the results of CRMNIST 164E using ICP-MS Thermo-Fisher Scientific Series II

Element	Unit	LOD	LOQ	Certified value	Average measured value ($n = 2$)	Recovery (%)
Na	mg/L	0.005	0.017	20.23	19.99	99
Mg	mg/L	0.001	0.004	7.841	7.847	100
K	mg/L	0.007	0.023	1.984	2.0315	102
Ca	mg/L	0.005	0.016	31.50	31.185	99
Al	µg/L	0.188	0.626	138.33	138.35	100
Ti	µg/L	0.013	0.043	na	na	na
V	µg/L	0.006	0.019	36.93	36.435	99
Cr	µg/L	0.012	0.041	19.9	19.625	99
Mn	µg/L	0.010	0.034	38.02	36.805	97
Fe	µg/L	0.074	0.246	95.70	93.525	98
Co	µg/L	0.002	0.007	26.40	25.01	95
Ni	µg/L	0.013	0.043	60.89	56.905	93
Cu	µg/L	0.016	0.054	22.20	21.165	95
Zn	µg/L	0.099	0.330	76.50	67.28	88
As	µg/L	0.070	0.233	58.98	53.09	90
Se	µg/L	0.025	0.084	11.68	10.175	87
Rb	µg/L	0.005	0.016	13.8	13.695	99
Sr	µg/L	0.019	0.063	315.20	314.3	100
Mo	µg/L	0.049	0.163	118.50	120	101
Cd	µg/L	0.003	0.008	6.408	6.0225	94
Cs	µg/L	0.002	0.005	na	na	na
Ba	µg/L	0.034	0.115	531.00	522.95	98
Pb	µg/L	0.003	0.008	19.15	17.795	93
U	µg/L	0.001	0.004	na	na	na

na not available

(PlasmaCAL, SCP Science, France) was used to create Ca, Mg, Na and K standards in the range 0–30 mg/L (0, 10, 20, 30 mg/L). Ti was determined semi-quantitatively.

Plasmalab software (version 2.5.4, Thermo-Fisher Scientific) was used for sample processing by an average calibration from two blocks, run before and after samples. Internal cross-calibration was applied.

Ion chromatography

Anions (Cl^-, F^-, SO_4^{2-} and NO_3^-) were measured with a Metrohm 850 Professional IC. The IC was equipped with a Metrosep A Supp 7—250/4.0 column, self-regenerating suppressor that used sodium carbonate (3.6 mM) eluent with a flow rate of 0.8 ml/min and conductivity detection. The recording time was 31 min, pressure was 10.36 MPa and the operating temperature was 45 °C. MagIC Net software was used for the calculations. The calibration standards were in the range (0, 10, 20 and 40 mg/L for Cl^- and NO_3^-), 0, 1, 2, and 3 mg/L for F^- and 0, 20, 40 and 60 mg/L for SO_4^{2-}. Recoveries for random blind samples ($n = 3$) were 106, 90, 104 and 111 % of Cl^-, F^-, SO_4^{2-} and NO_3^-, respectively.

Quality control

Several blanks were included in the measurement process to assess quality control, which included checking with international certified water standard reference material and in-house standard measurements.

The ICP-MS performance was checked for sensitivity [using Lithium (Li), Indium (In) and Uranium (U)], stability (using CeO/Ce ratio and Ba^{2+} ions) and the background signal in standard mode before converting to 'Collision Cell technology with Kinetic Energy Discrimination' mode (CCT-KED). Ten operational blanks were run to determine the limits of quantification ($LOQ = 10 \times SD$), and three replicates were used for limits of detection ($LOD = 3 \times SD$). Two samples of the CRM NIST 1643E (trace elements in water) were run after the 10 operational blanks for quality assurance (QA) purposes. The results of limit of detection (LOD), limit of

Table 3 WHO and SAS guideline values for drinking water

Organization		WHO (2008)	USEPA (2009)	GSO (2008)	SASO (SASO 1984/409)
Parameter	Unit	Guideline value	Guideline value	Guideline value	Guideline value
pH		6.5–9.5	6.5–8.5	–	6.5–8.5
EC	µS/cm	–	–	–	800–2,300
TH	mg/L	500	–	–	500
TDS	mg/L	1,000	500	–	1,500
F^-	mg/L	1.5	4	1.5	0.6–1.0
Cl^-	mg/L	250	250	–	600
NO_3^-	mg/L	50	10	50	45
SO_4^{2-}	mg/L	500	250	–	400
Na	mg/L	200	–	–	–
Mg	mg/L	–	–	–	30–150
K	mg/L	–	–	–	–
Ca	mg/L	–	–	–	200
Al	µg/L	200	50–200	–	–
Ti	µg/L	–	–	–	–
V	µg/L	–	–	–	–
Cr	µg/L	50	100	50	–
Mn	µg/L	400	50	400	50
Fe	µg/L	300	300	–	1,000
Co	µg/L	–	–	–	–
Ni	µg/L	70	–	70	–
Cu	µg/L	2,000	1,300	1,000	–
Zn	µg/L	3,000	5,000	–	–
As	µg/l	10	10	10	–
Se	µg/L	10	50	10	–
Rb	µg/L	–	–	–	–
Sr	µg/L	–	4.2 mg/L[a]	–	–
Mo	µg/L	70	–	70	–
Cd	µg/L	3	5	3	–
Cs	µg/L	–	–	–	–
Ba	µg/L	700	2,000	700	–
Pb	µg/L	10	15	10	–
U	µg/L	15	30	15	–

[a] AWWA (2014a, b)

quantification (LOQ) and certified reference material (CRM) from National Institute for Standards and Technology (NIST); CRM NIST1643e are shown in Table 2.

Results

The guideline values of WHO, USEPA, GSO and SASO (WHO 2008; USEPA 2009; GSO 2008; SASO 1984) for drinking water are summarized in Table 3. A summary of the parameters (Physicochemical properties and the concentration of anions, major and trace elements) for the three types of water samples (ground water treated drinking water and bottled drinking water) is shown in Table 4. Levels of all parameters are presented in mean, standard deviation (SD), minimum (Min) and maximum (Max).

Figure 1 shows comparison of the levels of major elements, anions and physicochemical properties in bottled drinking water, between labeled values (mean) and measured values (mean).

Discussion

Physiochemical properties

The average pH for ground water was slightly lower than the average values recorded for both treated drinking water

Table 4 Summary of the parameters measured in different water samples collected from Najran city

Sample		Groundwater ($n = 11$)				Treated drinking water ($n = 13$)				Bottled drinking water ($n = 24$)			
Parameter	Unit	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD
pH		7.12	7.82	7.59	0.21	7.19	8.41	7.84	0.40	7.50	8.32	7.97	0.20
EC	µS/cm	536.00	339.00	1,090.00	815.00	119.40	387.00	236.19	88.41	97.20	605.00	271.59	94.98
TH	mg/L	201.10	1,252.30	406.17	303.17	14.20	143.60	73.44	40.35	18.67	276.68	75.72	56.92
TDS	mg/L	104.00	1,290.00	418.73	321.85	31.00	171.00	99.23	44.17	42.00	249.00	117.71	38.44
F^-	mg/L	nd	0.80	0.30	0.25	nd	0.31	0.11	0.13	nd	1.49	0.73	0.46
Cl^-	mg/L	23.00	364.00	96.86	104.58	0.30	29.00	10.96	7.63	0.30	86.00	22.02	20.46
NO_3^-	mg/L	1.00	25.00	11.82	6.51	5.00	23.00	9.46	4.89	nd	15.00	5.50	3.67
SO_4^{2-}	mg/L	4.00	1,132.00	190.73	316.61	5.00	55.00	28.15	15.12	0.11	85.00	28.88	24.51
Na	mg/L	17.13	108.20	35.59	26.64	4.19	22.27	9.62	4.93	1.66	52.85	18.69	13.81
Mg	mg/L	10.19	62.01	21.17	15.16	0.70	7.28	3.73	1.97	0.30	27.06	7.19	7.26
K	mg/L	3.68	8.49	4.90	1.37	0.82	3.05	1.83	0.79	0.04	6.49	1.10	1.28
Ca	mg/L	63.72	399.30	127.76	96.61	4.52	45.50	22.94	12.92	0.24	66.20	17.22	16.31
Al	µg/L	<LOQ	3.20	1.32	0.81	<LOQ	3.65	1.53	0.94	<LOQ	8.67	2.49	2.15
Ti	µg/L	<LOQ	0.06	<LOQ	0.01	<LOD	<LOQ	<LOQ	0.01	<LOD	0.08	<LOD	0.02
V	µg/L	3.86	4.59	4.24	0.26	0.18	3.32	1.46	0.99	0.02	10.59	1.05	2.27
Cr	µg/L	<LOD	2.88	1.57	0.72	<LOQ	0.61	0.30	0.19	<LOD	1.15	0.24	0.29
Mn	µg/L	<LOD	1.25	0.18	0.38	<LOD	0.36	0.10	0.12	<LOD	6.79	0.46	1.36
Fe	µg/L	<LOD	1.48	0.54	0.40	<LOD	4.72	0.59	1.27	<LOD	2.94	0.51	0.61
Co	µg/L	0.01	0.09	0.02	0.02	0.00	0.04	0.01	0.01	<LOD	0.13	0.02	0.03
Ni	µg/L	<LOD	1.82	0.31	0.53	<LOD	1.47	0.23	0.39	<LOD	2.33	0.15	0.47
Cu	µg/L	<LOD	17.73	1.73	5.31	0.07	1.61	0.54	0.48	<LOD	1.36	0.06	0.28
Zn	µg/L	<LOD	587.80	94.10	182.65	3.23	200.60	28.39	52.49	<LOD	14.79	2.98	3.91
As	µg/l	0.95	1.66	1.26	0.25	<LOD	1.02	0.43	0.32	<LOD	3.99	0.28	0.81
Se	µg/L	1.00	6.42	2.83	1.40	0.11	0.63	0.35	0.19	<LOD	0.99	0.19	0.24
Rb	µg/L	0.41	1.16	0.62	0.25	0.12	1.00	0.30	0.24	0.02	5.76	0.59	1.16
Sr	µg/L	377.30	2,728.00	848.03	695.59	29.17	276.10	138.34	76.45	0.75	365.90	74.82	89.76
Mo	µg/L	0.57	1.42	1.08	0.27	<LOQ	1.61	0.65	0.51	<LOQ	1.49	0.22	0.34
Cd	µg/L	<LOD	0.10	0.01	0.03	<LOD	0.01	<LOD	0.00	<LOD	0.01	<LOD	0.00
Cs	µg/L	<LOD	<LOD	<LOD	0.00	<LOD	<LOD	<LOD	0.00	<LOD	0.06	0.01	0.01
Ba	µg/L	27.51	139.30	53.54	32.29	1.39	17.58	8.28	4.91	<LOQ	331.80	20.53	69.81
Pb	µg/L	<LOD	0.14	0.01	0.04	<LOD	0.09	0.01	0.03	<LOD	0.02	<LOD	0.00
U	µg/L	1.81	6.13	3.44	1.27	0.02	1.61	0.60	0.53	<LOD	1.92	0.21	0.43

nd not detected

and bottled drinking water (Table 4). The difference may be due to the coagulant material used for water purification. The pH of the treated drinking water samples' range overlaps with the range for bottled drinking water samples, and is within the WHO guidelines (WHO 2008), including the ground water samples. Average pH values for drinking water in this study were generally higher than those for groundwater samples, indicating a positive outcome from water treatment processes and/or the presence of carbonate. Drinking water pH values should be controlled at all stages of water treatment and distribution to avoid any harmful effects to human health, and to minimize corrosion of water distribution systems (WHO 2003a).

In ground water, the average values of EC, TH and TDS were very high compared with those obtained for treated drinking water and bottled drinking water samples (Table 4). The TH was calculated from Ca to Mg concentrations, which are the highest in ground water samples. The TDS and EC values have correlation, as a rough rule one ppm of TDS correlates to a conductivity of two µS/cm (Hydranautics 2014). The mean value of TDS in ground water samples is approximately fourfold compared to mean values recorded for treated drinking water samples and bottled drinking water samples (Table 4). The mean values of the EC, TH and TDS in treated drinking water samples were the lowest, which may be due to the softening

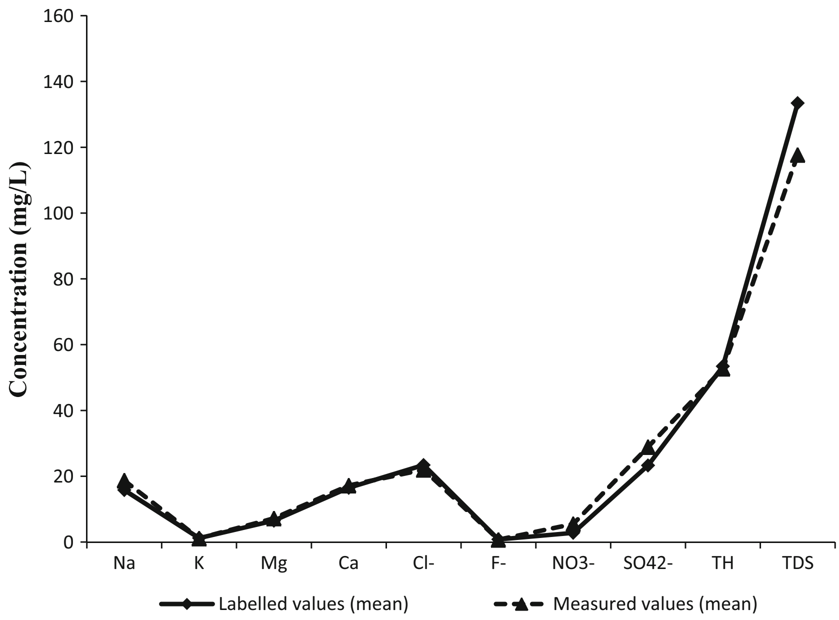

Fig. 1 Comparison of the levels of major elements, anions and physicochemical properties, in bottled drinking water, between labeled values (mean) and measured values (mean)

process. This also may be attributed to ion removal during the treatment process. The values of EC, TH and TDS in both types of drinking water samples were much lower than those recommended by the SASO (1984) and WHO (2008) guidelines (Table 3). It is worth mentioning that some TH and TDS values for ground water samples (three samples only) exceeded the guideline values set by WHO (2008).

Anions

As shown in Table 4, average concentrations of anions (F$^-$, Cl$^-$, NO$_3^-$ and SO$_4^{2-}$) in ground water were higher than those in both treated drinking water and bottled drinking water samples. The following range of concentrations for anions (Cl$^-$, NO3$^-$ and SO$_4^{2-}$ (10–100 mg/L) and F$^-$ (0.1–1 mg/L) in drinking water is considered essential for human health (Foster et al. 2006). One sample among the ground water samples had the highest average concentrations for Cl$^-$ (364 mg/L). The highest value of Cl$^-$ was below SASO guideline value, and higher than WHO and USEPA guideline values. However, the anions' levels in the rest of the samples were below the national and international guideline thresholds (Table 3).

The average Cl$^-$ concentration in bottled drinking water was almost twice that of treated drinking water, and showed greater variation than that of treated drinking water (Table 4). There are different sources (brands—different aquifers) of bottled drinking water while treated drinking water samples came from one source (Najran valley—same aquifer). Despite this variation, the Cl$^-$ concentrations in both types of drinking water do not exceed the international and national guideline values (Tables 3, 4). It is noteworthy that, to date, no health-based values have been proposed for Cl$^-$ in drinking water (WHO 2003b).

Only one sample among the ground water samples had high concentration for SO$_4^{2-}$ (1132 mg/L), exceeding the recommended values for all organizations. If SO$_4^{2-}$ concentrations in drinking water are high, there is a noticeable taste, and concentrations of 1000–1200 mg/L have a laxative effect on humans. However, there is no health-based guideline value for SO$_4^{2-}$ in drinking water (WHO 2004). SO$_4^{2-}$ concentrations in both types of drinking water were below the USEPA (2009), WHO and SASO (1984) guideline values.

Occurrence of F$^-$ and concentrations in samples varied to such a degree that samples fell into two distinct groups. F$^-$ was not detected in seven of the treated drinking water samples ($n = 13$), and four of the bottled drinking water samples ($n = 24$). However, the fact that the F$^-$ ion is present in all but two ground water samples, the source of the treated drinking water, suggests that this anion is depleted by the treatment processes. These findings agree with results of a recent study that reported average F$^-$ concentrations of 0.35–0.82 mg/L in ground water in Najran area (Alabdulaaly et al. 2013). More importantly, our data suggest that the population of Najran, even if only ingesting 3L of the available drinking water daily, is exposed to low levels of F$^-$. Indeed, the drinking water intake requirements for adults in normal conditions are in the range 2.5–3 L/d; in hot climates, it is greater than 3L/d (Popkin et al. 2010), while in a fluoridated area in a temperate climate, the daily intake of fluoride in drinking water is 0.6 and 2 mg/adult (Fawell et al. 2006). It is very difficult to find a study on the adverse health effects associated with fluoride deficiency in drinking water. Dean et al.

(1939) showed that, in areas where fluoride levels in drinking water were low; there was a high incidence of dental caries. Further, side effects from a fluoride-deficient diet include weak bones and teeth and increased cavities (MedlinePlus 2014). Conversely, several other studies, undertaken in 28 different countries worldwide, have indicated that exposure to high drinking water fluoride concentrations is associated with human dental fluorosis (Fawell et al. 2006). In particular, studies carried out by Akpata et al. (1997) and Albdulaaly et al. (2013) in the Hail region of the KSA reported incidences of dental fluorosis among children, and well water fluoride concentrations ranging between 0.3 and 4.0 mg/L. Another series of (more than 20) papers concluded that children exposed to high levels of fluoride in drinking water had lower IQs (Choi et al. 2012).

NO_3^- in drinking water come from environmental (geogenic) and anthropogenic sources, and include runoff from fertilizer, municipal sewage treatment systems, leaching from septic tanks, erosion of natural deposits and animal wastes (Ricker et al. 2001; EPA 2009). High NO_3^- concentrations in drinking water reflect contamination of water sources (Azrina et al. 2011). The measured concentrations of NO_3^- in all three types of water samples did not exceed the guideline values set by SASO, GSO and WHO. However, only three samples from both treated drinking water and bottled drinking water samples were exceeded the threshold of the USEPA (2009). Moreover, seven samples from ground water samples were also exceeded the guideline value of USEPA (Table 3).

Major elements

Actually the major elements with the range of concentrations Na and Ca (10–100 mg/L) Mg and K (1–10 mg/L) in drinking water are considered as essential to human health (Foster et al. 2006). In this study, the measured average concentrations of these major elements in ground water were higher than those for both treated drinking water and bottled drinking water (Table 4). These differences suggest that these elements are significantly depleted during the water treatment processes. The treatment seems to determine the element concentration ratios, as bottled drinking water has lower K and Ca concentrations, and higher Na and Mg concentrations, than treated drinking water. The measured concentrations for all major elements in all samples did not exceed the national and/or international guideline limits. Except only one sample for Ca concentration, among ground water samples, was exceeded the limit values for all organizations. Likewise, this sample was the same sample that recorded higher values for Cl^-, SO_4^{2-}, NO_3^-, TDS, TH and EC as previously mentioned.

Trace elements

Only 1 % of naturally occurring dissolved constituents in groundwater is made up of trace elements. The trace elements are divided into two categories with range of concentrations—essential to human health: V, Se, Co, Ni and Cr (0.1–1 µg/L), Ba, Cu and Mn (1–10 µg/L), Fe and Zn (10–100 µg/L) and Sr (100–1000 µg/L); toxic elements: As, Cd, Pb and Al (0.1–1 µg/L), U (1–10 µg/L). (Foster et al. 2006).

The above-mentioned sample (ground water sample) that recorded higher values for Cl^-, SO_4^{2-}, NO_3^-, TDS, TH and EC was also recorded highest value for Sr. In this case, Sr value did not exceed the recommended value (AWWA 2014a, b, Table 3). The concentrations of trace elements for the three types of water samples are presented in Table 4. Mean concentrations of 20 trace elements in the three types of the tested water samples were very low and did not exceed the guideline values of all organizations. Ground water samples were recorded higher values for V, Cr, Ni, Cu, Zn, As, Sr, Mo, Ba, Se and U than both treated drinking water samples and bottled drinking water samples. The presence of V, As, Sr, Mo, Ba and U in ground water was not surprising, because these elements are naturally occurring elements (WHO 2008; AWWA 2014a). Nevertheless, the occurrence of Cr, Ni, Cu and Zn could be due to containers and distributing system. Previous study reported that Cd, Fe, Cu and Zn in drinking water samples may be the result of these elements leaching from the storage tanks and/or distribution pipes (Al-Saleh and Al-Doush 1998). Fortunately, groundwater was not used for drinking purpose. This can be avoided by improving the water distribution system and by regular maintenance. At lower levels, these elements are considered safe, as shown in Table 3. Some elements such as Ti, Cd, Cs and Pb were less than LOQ for all tested water samples. This is promising because these elements considered to be toxic and could pose risk to human health (Foster et al. 2006; Holbrook et al. 2013). Fe and Co values were very low, just twice as LOQ for each element, in all tested samples. Both elements are considered essential to human health in drinking water with the following range of concentrations [Co (0.1–1 µg/L) and Fe (10–100 µg/L)] (Foster et al. 2006). Therefore, adequate quantity of these elements can not be obtained from such drinking water tested in this study. The range of mean values (1.3–2.5 µg/L) for Al was found to be in the following order: treated drinking water > bottled drinking water > groundwater. This measured range of Al in all tested samples is 80 times lower than the guideline set by WHO (2008) in drinking water. Thus, this is a promising result for such a toxic element in drinking water. The highest average value (0.5 µg/L) for Mn was recorded in bottled drinking water samples. Thus far, this measured value is lower than the essential level of Mn in drinking water. Average values of Rb were reported very low in all tested water samples. The values were far below the lower limit for Rb level (0.1–100 µg/L) in natural groundwater FWQP (2003).

The Sr in naturally occurring element and the guideline value (4200 µg/L) for Sr is very high as shown in Table 3, compared to all trace elements, except for Zn, Cu and Fe. The increasing order of Sr-measured values is ground water > treated water > bottled water, which explain that the geographic However, the recorded values in all three water types did not exceed the guideline value.

The Sr mean value (74.82 µg/L) of this study in bottled drinking water was not high compared to other studies, median (179 µg/L) in bottled drinking water and median of European bottled water (406 µg/L) and mean of Sicilian bottled natural waters (298 µg/L) area is the source of this element. (Birke et al. 2010; Varrica et al. 2013). The reported average value of Sr in ground water and treated water samples could be attributed to the geogenic source of the water.

Groundwater could have good benefit after selective removal of harmful substances. This is because the ground water samples showed high levels of essential elements such as Zn and Se.

Zn is an essential element to humans and other living organisms, in terms of enzymatic function. Approximately, 200 zinc-containing enzymes have been identified, including dehydrogenases, phosphatases, peptidases and polymerases (WHO 1996; O'Dell 1984). Recommended Dietary Allowances (RDAs) for Zn are 8 and 11 mg for adult females and males, respectively (NIH 2014). The average daily intake for an adult from ground water source in Najran is calculated as 282.3 µg, if the adult ingested up to 3 L water per day.

Selenium (Se) is an essential element for humans. Therefore, the recommended daily intakes of Se were jointly set by World Health Organization and Food and Agriculture Organization as 26 µg per day for adult females and 35 µg of Se per day for adult males (WHO 2011). Based on the results of this study, the mean of Se in ground water samples is 2.83 µg/L (Table 4). Our data suggest that if an adult in Najran ingested 3 L of ground water per day, the daily intake will be 8.5 µg. This daily intake will be third of the recommended daily value for adult women and forth of the recommended daily value for adult males.

Results show that the drinking water quality in Najran generally meets the international standards. Toxic elements such as Cd, Al, As, and Pb were either present in minute quantities or not detectable at all, and were below the WHO, USEPA and GSO guideline values. As such, human consumption of treated drinking water or bottled drinking water in Najran should not lead to adverse health effects typically associated with these elements. The levels of trace elements in the bottled and treated drinking water samples do not suggest any implications for human health, based on international/national guideline values (Tables 3, 4).

It is noteworthy that none of the measured elements in drinking water samples in this study exceeded the international guideline values. Therefore, one can conclude that the drinking water quality in Najran city complies with international guidelines.

Quality measurement for bottled drinking water

Comparison of label contents, in all bottled drinking water samples, was established with measured values in this study (Fig. 1). A good agreement showed between average values of parameters on the labels of bottled water and measured parameters in this work. This provides reliable information on labels of bottled drinking water. However, TDS average value was slightly higher for measured results than the reported values on labels. This may be due to reporting the TDS values on bottles' labels as range in some bottles rather than one single value.

Conclusions

Based on all measured parameters, drinking water quality in Najran city complies with national and international standards. However, some essential elements for human health such as fluoride iron and cobalt either hardly detected or near to limit of quantification. Fluoride was not detected in 53.8 % samples of treated drinking water and 16.7 % samples of bottled drinking water. Ion and cobalt cannot be quantified in 61.5 and 46.2 % of treated drinking water samples, 33.3 and 25 % of bottled drinking water samples, respectively.

Drinking water in Najran city should be given careful attention, especially for F^-, Fe and Co in treated drinking water. This study is important as it will increase public awareness and knowledge about drinking water, and also serves as a contribution to, and promotion of, public health. More and regular studies are recommended, in this field, to enrich the demonstrated information in this study about the drinking water.

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References

Akpata ES, Fakiha Z, Khan N (1997) Dental fluorosis in 12–15-year-old rural children exposed to fluorides from well drinking water in the Hail region of Saudi Arabia. Community Dent Oral Epidemiol 25:324–327

Al Nouri D, Al Abdulkarim B, Arzoo S, Bakeet ZA (2014) Quality characteristics of commonly consumed drinking water in Riyadh and effect of domestic treatments on its chemical constituents. J Food Nutr Res 2:25–33. doi:10.12691/jfnr-2-1-5

Alabdulaaly AI, Al-Zarah AI, Khan MA (2013) Occurrence of fluoride in groundwaters of Saudi Arabia. Appl Water Sci 3:589–595

Al-Saleh I, Al-Doush I (1998) Survey of trace elements in household and bottled drinking water samples collected in Riyadh, Saudi Arabia. Sci Total Environ 216:181–192

APHA (1999) Standard methods for the examination of water and wastewater, 20th edition. American Public Health Association, Washington, DC. www.mwa.co.th/download/file_upload/SMWW_1000-3000.pdf. Accessed 16 Aug 2014

Avino P, Capannesi G, Rosada A (2011) Ultra-trace nutritional and toxicological elements in Rome and Florence drinking waters determined by Instrumental Neutron Activation Analysis. Microchem J 97:144–153

AWWA (2014) The Potential Regulatory Implications of Strontium. American Water Works Association www.awwa.org/Portals/0/files/…/2014AWWAStrontiumBriefingPaper.pdf. Accessed 17 Aug 2014

AWWA (2014a) Vanadium. American Water Works Association http://www.drinktap.org/home/water-information/water-quality/ucmr3/vanadium.aspx. Accessed 17 Aug 2014

Azrina A, Khoo HE, Idris MA, Amin I, Razman MR (2011) Major inorganic elements in tap water samples in Peninsular Malaysia. Mal J Nutr 17:271–276

Barati AH, Maleki A, Alasvan M (2010) Multi-trace elements level in drinking water and the prevalence of multi-chronic arsenical poisoning in residents in the west area of Iran. Sci Total Environ 408:23–1529

Birke M, Reimann C, Demetriades A, Rauch U, Lorenz H, Harazim B, Glatte W (2010) Determination of major and trace elements in European bottled mineral water-Analytical methods. J Geochem Explor 107:217–226

Bryant G, McPhilliamy S (2002) Final report: a survey of the water quality of streams in the primary region of mountaintop/valley fill coal mining. www.cet.edu/pdf/mtmvfchemistry.pdf. Accessed 16 Aug 2014

Choi AL, Sun G, Zhang Y, Grandjean P (2012) Developmental fluoride neurotoxicity: a systematic review and meta-analysis. Environ Health Perspect 120:1362–1368

Da Silva MAM, Frescura VLA, Curtius AJ (2000) Determination of trace elements in water samples by ultrasonic nebulization inductively coupled plasma mass spectrometry after cloud point extraction. Spectrochim Acta Part B 55:803–813

Datamonitor (2014) BottledWater - Global Industry Guide. http://www.datamonitor.com/store/Product/bottled_water_global_industry_guide?productid=ML00016-019. Accessed 16 Aug 2014

Dean HT, Jay P, Arnold FA Jr, McClure FJ, Elvove E (1939) Domestic water and dental caries, including certain epidemiological aspects of oral L. acidophilus. Public Health Rep 54:862–888

Dinelli E, Lima A, Albanese S, Birke M, Cicchella D, Giaccio L, Valera P, De Vivo B (2012) Major and trace elements in tap water from Italy. J Geochem Explor 112:54–75

EPA (2009) An alphabetical listing with links to fact sheets on the primary drinking water regulations. http://water.epa.gov/drink/contaminants/index.cfm. Accessed 23 March 2013

Fawell J, Bailey K, Chilton J, Dahi E, Fewtrell L, Magara Y(2006) Fluoride in drinking-water. World Health Organization

Foster S, Kemper K, Tuinhof A, Koundouri P, Nanni M, Garduño H (2006) Natural Groundwater Quality Hazards, avoiding problems and formulating mitigation strategies. GW.MATE Core Group. Briefing Note Series Note 14. www.un-igrac.org/dynamics/modules/SFIL0100/view.php?fil_Id=175. Accessed 19 Aug 2014

FWQP (2003) Groundwater quality and groundwater pollution. Farm Water Quality Planning (FWQP). http://groundwater.ucdavis.edu/files/136273.pdf. Accessed 20 Aug 2014

GSO (2008) GCC Standardization Organization (GSO). Unbottled drinking water, Standard. No. 149/2000

Hashem AR (1993) Heavy metals analysis of water and soils from Saudi Arabia. J King Saud Univ Sci 5:39–46

Holbrook RV, Motabar D, Quiñones O, Stanford B, Vanderford B, Moss D (2013) Titanium distribution in swimming pool water is dominated by dissolved species. Environ Pollut 181:68–74

Hydranautics (2014) RO water Chemistry. www.membranes.com/docs/papers/04_ro_water_chemistry.pdf. Accesssed 20 Aug 2014

Khanfar AR (2010) Dissolved nitrogen in drinking water resources in Al-Mahareth village of Assir–Saudi Arabia. Saudi J Biol Sci 17:265–268

Lee K, Oshima M, Takayanagi T, Motomizu S (1999) Determination of trace with elements in water samples by Inductively coupled plasma- mass spectrometry connected air flow- and water flow-injection techniques. J Flow Injection Anal 16:255–264

MedlinePlus (2014) Fluoride in diet. http://www.nlm.nih.gov/medlineplus/ency/article/002420.htm. Accessed 15 Jan 2014

NIH (2014) National Institutes of Health. Zinc Fact Sheet for Health Professionals. http://ods.od.nih.gov/factsheets/Zinc-HealthProfessional/. Accessed 20 Oct 2014

O'Dell BL (1984) History and status of zinc in nutrition. Fed Proc 43:2821–2822

Popkin BM, D'Anci KE, Rosenberg IH (2010) Water, hydration and health. Nutr Rev 68:439–458

Reimann C, Bjorvatn K, Frengstad B, Melaku Z, Tekle-Haimanot R, Siewers U (2003) Drinking water quality in the Ethiopian section of the East African Rift Valley I—data and health aspects. Sci Total Environ 311:65–80

Ricker J, Peters S, Golling R (2001) Evaluation of Urban water quality In: Task 4 Report. San Lorenzo River watershed management plan update. www.scceh.com/LinkClick.aspx?fileticket=RTXstB20rvI%3D&tabid=1690. Accessed 16 Aug 2014

SASO (1984) Water quality and standards, Chapter 3. 1984. uqu.edu.sa/files2/tiny_mce/plugins/filemanager/files/…/(ch)3.pdf. Accessed 27 Sep 2013

Stetzenbach KJ, Amano M, Kreamer DK, Hodge VF (1994) Testing the limits of ICP-MS: determination of trace elements in groundwater at part- per- trillion level. Groundwater 32:976–985

USEPA (2009) United States Environmental Protection Agency (USEPA), EPA 816-F-09-004

Varrica D, Tamburo E, Dongarrà G (2013) Sicilian bottled natural waters: major and trace inorganic components. Appl Geochem 34:101–113

WHO (1996) Zinc in drinking-water, WHO/SDE/WSH/03.04/17

WHO (2003a) pH in drinking-water, WHO/SDE/WHO/03.04/12

WHO (2003b) Chloride in drinking-water. WHO/SDE/WSH/03.04/16

WHO (2004) Sulfate in drinking, WHO/SDE/WSH/03.04/114

WHO (2008) Guidelines for Drinking-water Quality, 3rd ed. Incorporating the first and second addenda, Vol 1, Recommendations, World Health Organization, Geneva

WHO (2011) Selenium in drinking-water, WHO/HSE/WSH/10.01/14