Article

Nitrate and arsenic concentration status in Zamzam water, Holly Mecca Almocarama, Saudi Arabia

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Abstract

Many Muslims people drink Zamzam water either for medicinal or religious purpose; however, some study recorded that the water is contaminated by nitrate and arsenic. The main objective of this investigation is to evaluate the water for drinking focusing on nitrate and arsenic. The chemical, total dissolved salts (TDS), major, minor and trace elements, and microbial, total colony counts, total coliforms group, and *E.coli*, analyses were carried out and compared with WHO standards. The acquired results recorded that the TDS, soluble ions, trace element including As and NO_3^- fall within the acceptable limits. Furthermore, the water found free of total colony counts (CFU) and *E. coli* contaminations. On the other hand, 6.9% of the studied water found contaminated with total Coliform group. This study found lithium ion in high concentration with an average of 0.184 mg L^{-1} in studied water. Although no maximum contamination level set for lithium either by WHO or EPA; however, many studies confirmed that the lithium can decrease the incidence rates of suicide, homicide, and rape.

Keywords Zamzam; groundwater quality; Mecca; arsenic; Nitrate.

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1 Introduction

It is needless to say that the drinking water quality is the most important issues to human health all over the world. About 70% of an adult's total body weight is water; without it in a consistent range, the body's survival time is restricted (Al-Omran et al., 2013). Drinking water is defined as the water pure enough to be used with low immediate or long-term hazards. In many parts of the world especially in arid environment, people have to use water either contaminated with disease vectors, pathogens, or unacceptable levels of toxins and suspended solids (William and Frank, 2000). Using this water undoubtedly leads to numerous diseases and in some time death in many countries. Consequently, the decrease of waterborne diseases is a main public health objective in recent years. The periodical analysis of the drinking groundwater water is necessary to ensure its safety (U.S.

Environmental Protection Agency (USEPA, 2007). The chemical and microbial analyses of groundwater have an imperative role in evaluating and assessing the quality water (Tiwari, 2011). The Kingdom of Saudi Arabia (KSA), located in arid environment, depends mainly on the groundwater, a main sources of water (Al-Omran et al. 2013). The KSA's groundwater is deteriorating in alarming way due to increase salinity. The average electrical conductivity had been dramatically increased from 1.93 dS m^{-1} in 1983 to more than 3.2 dS m^{-1} in 2013 for Saq Aquifer in KSA; furthermore, some wells in Saq aquifer its salinity increased to reach 9.7 dS m^{-1} (Al-Omran et al., 2013). Most basalt covered areas in western part of KSA contain poor quality water (Sharaf and Hussein, 1997). Nevertheless, this part of KSA include Zamzam well, a Muslims holly well, which millions of Muslims people and pilgrims drink its water from long time ago (~ 4000 years) (Khalid et al., 2014). Al-Gamal (2009) recorded that the recharge of Zamzam well may be occurred during the last Holocene humid period and that the aquifer is now discharging ancient groundwater resources. Shomar (2012) reported that the top 14 m of the Zamzam well is excavated in the sandy alluvium of the Wadi Ibrahim; however, the lower 17 m is located in the diorite bedrock. A 0.5 m thick of highly permeable weathered rock located between the alluvium and bedrock. Most of the alluvial section of the well is lined with stone except for the uppermost 1 m, which has a reinforced concrete collar. Muslims people drink Zamzam water either for medicinal or religious purpose (Shomar, 2012). The long residence time with aquifer materials of basic lava origin (basalt) lead to the ferro-magnesium minerals formation from the soluble calcium and magnesium in water (Al-Gamal, 2009). Shomar (2012) stated that the Zamzam water is contaminated by As and NO_3; however, Al Nouri (2014) reported that the Zamzam water is free of As and NO_3^- contaminations. Griffin et al. (2007) said that the Zamzam water contain high concentration of Fluoride and some other element. Mashat (2010) reported that the Zamzam water has no microbial contamination due to it is naturally pure and sterilized by salts contents. This study aims at investigating the suitability of Zamzam water for drinking purpose.

2 Study Area and Methodology

2.1 Study site

Holly city of Mecca is situated in the western part of KSA about 70 km far away from Jeddah city near Red Sea (Fig. 1). The holly city is located in latitudes 21º 26' 48" N and longitudes 39º 53' 46" E with an elevation ~ 426.4 m above mean sea level (Al-Gamal, 2009) (Fig. 1). The Holly city contains AlMsgied Alharam (Fig. 2). The Ka'ba Amosharafa is located inside the Alharam and the Zamzam well located at about 20 Meters east of the Ka'ba (Fig. 2). The Zamzam well is about 30.5 m deep, with an interior diameter ranging between 1.08 to 2.66 meters (Koshak, 1983).

2.2 Sample collection

In this study, 29 Zamzam water samples were collected from different locations inside the Holy Haram in Mecca Al-Mocarama and from original wells (Fig. 1 and Table 1) during the year 2015. All samples were stored in icebox and transport to King Saud University's labs for analysis.

2.3 Microbiological analysis

The total numbers of colony in the studied water were determined by nutrient agar method; however, the Coliforms group and *E. coli* were determined by Colilert (defined substrate) method as described by Eckner (1998); and Maheux et al. (2008).

2.4 Chemical analysis

The samples were analyzed for electrical conductivity (EC) in dS/m and pH using EC meter at 25 WC (Test kit Model 1500-20, Cole and Parmer) and pH meters (CG 817), respectively. Furthermore, Ca^{2+}, Mg^{2+}, Na^+, Li^+, K^+, Cl^-, SO_4^{2-}, NO_3^-, and NO_2^-, were determined using Ion Chromatography System (ICS 5000, Thermo

(USA)). The CO_3^{-2} and HCO_3^- concentration were determined by titration using sulfuric acid. The As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn were measured using ICP-Perkin Elmer Model 4300DV (Matiti, 2004).

Fig. 1 Location of Mecca Alocarama.

Fig. 2 General view of AlMsgied Alharam, contain Ka'pa Almosharafa and Zamzam well, in the heart of Mecca.

Table 1 Zamzam samples location in Mecca Alomcrama and total coliform.

Sample No	Description	Type	Total Coliform
1	Inside Al-Haram	Ice box	(-)
2	Inside Al-Haram	Ice box	(-)
3	Inside Al-Haram	Ice box	(++)
4	Inside Al-Haram	Ice box	(-)
5	Inside Sahn	Ice box	(-)
6	Inside Sahn	Ice box	(-)
7	Inside Sahn	Ice box	(-)
8	Inside Sahn	Ice box	(-)
9	Inside Al-Haram	Ice box	(-)
10	Inside Al-Haram	Ice box	(-)
11	Inside Masa	tap	(-)
12	Inside Masa	tap	(-)
13	Inside Masa	tap	(-)
14	Inside Masa	tap	(-)
15	Inside Masa	tap	(-)
16	Inside Masa	tap	(-)
17	Inside Al-Haram	tap	(-)
18	Inside Al-Haram	tap	(-)
19	Inside Al-Haram	tap	(-)
20	Outside Al-Haram	tap	(-)
21	Outside Al-Haram	tap	(-)
22	Outside Al-Haram	tap	(-)
23	Outside Al-Haram (Safa)	tap	(+++)
24	Main sources	tap	(-)
25	Main sources	tap	(-)
26	Main sources	tap	(-)
27	Zamzam water company	Bottled water	(-)
28	Zamzam water company	Bottled water	(-)
29	Zamzam water company	Bottled water	(-)

3 Results and Discussion

3.1 Microbial assessment

The non-pathogenic microorganisms such as total coliforms, *E. coli*, fecal streptococci and other pathogens can act as a bio-indicators of faecal pollution (Stevens et al., 2003). In this study two bio-indicators, total coliforms and *E. coli*, were used. The results showed that the Zamzam water is free of faecal pollution. All studied Zamzam waters were within the permissible limits with respect total colony counts (CFU) and *E. coli* (Table 2). The U.S. Environmental Protection Agency (2009) for microbial load is 500 CFU/ ml; however, the water considered unsuitable if contain only one cell of *E. coli.* Only two samples (6.9%) of studied waters were found unsuitable due to infections by total coliforms. The total coliforms numbers recorded in the two samples were 689.6 and 1986.3 (CFU / 100 ml); nonetheless, the remaining contain no total coliforms. This study suggest that the reason of the contamination of the three Zamzam water samples is the inconvenience behave of some pilgrims during drinking the water, i.e.: washing their hands and face, and not due to water

coming from the main source. The drinking waters coming from the main sources were found to be free from any microbial contamination including *E. coli* (Table 1) (Al-Omran et al., 2015).

Table 2 Descriptive statistics of Zamzam groundwater microorganisms (n=29).

Sample No	Total colony counts	Total coliforms (CFU/100ml)	*E. coli*
	(CFU / ml) x 10^2	(CFU / 100 ml)	(CFU / 100 ml)
Maximum	86	1986.3	Nil
Minimum	Nil	Nil	Nil
Mean	18.1	75.6	Nil
St. deviation	21.9	330.4	-
Variance	4.7	18.2	-
Standard error	0.3	0.5	-
Median	10.3	Nil	Nil
Skew	1.5	4.9	-

3.2 Chemical assessment

The statistical analysis of the groundwater was done to identify the chemical parameters that are deviating from WHO drinking water standard (Tables 3, 4, and 5). It was noted that the mean and maximum of most parameters in the studied groundwater found within the acceptable limits of the used standard (Table 3, 4, and 5) (Al-Omran et al., 2012; Aly et al., 2013; WHO, 2011; USEPA, 2009). In contract, most of groundwaters in KSA were unsuitable for drinking due to high salinity and/or contaminations (Aly et al., 2013)

Lithium, the alkali-metal group that includes sodium and potassium, is found in Zamzam water at high concentration with an average of 0.184 mg L^{-1} (Table 5). For drinking water, there is no current WHO or EPA maximum contamination level set for lithium. However, the incidence rates of suicide, homicide, and rape are found significantly higher in counties whose drinking water supplies contain little or no lithium than in counties with water lithium levels ranging from 70-170 μg/L (Schrauzer and Shrestha, 1990; Ohgami et al., 2009).

Fluorine is a common element that is widely distributed in Earth's crust and exists in the form of fluorides in a number of minerals, such as fluorspar, cryolite and fluorapatite. Traces of fluorides are present in many waters, with higher concentrations often associated with groundwaters (WHO, 2011). All vegetation contains some fluoride, which is absorbed from soil and water. Tea in particular can contain high fluoride concentrations, and levels in dry tea are on average 100 mg/kg. Fluoride is widely used in dental preparations to combat dental caries, particularly in areas of high sugar intake. These can be in the form of tablets, mouthwashes, toothpaste, varnishes or gels for local application. In some countries, fluoride may also be added to table salt or drinking-water in order to provide protection against dental caries. The amounts added to drinking-water are such that final concentrations are usually between 0.5 and 1 mg/L. The fluoride is found in

Zamzam water with adequate amount and within permissible limits of WHO. It was ranged between 0.87-1.59 mg/L with an average of 0.96 mg/L (Table 5).

Table 3 Descriptive statistics of Zamzam groundwater chemical composition (n=29).

Sample No	pH	EC	Cations (meq/L)				Anions (meq/L)			
		(dS/m)	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	CO_3^{--}	HCO_3^{-}	Cl^{-}	SO_4^{--}
Maximum	8.26	0.80	3.37	2.52	3.77	0.70	1.60	3.60	3.83	2.94
Minimum	8.05	0.77	2.88	1.93	2.92	0.39	0.00	2.20	2.86	2.35
Mean	8.19	0.79	3.14	2.15	3.42	0.46	0.79	3.11	3.23	2.55
St. deviation	0.05	0.01	0.13	0.12	0.19	0.05	0.38	0.35	0.16	0.08
Variance	0.23	0.10	0.36	0.35	0.44	0.23	0.61	0.59	0.41	0.29
St. error	0.06	0.04	0.08	0.08	0.08	0.06	0.10	0.10	0.08	0.07
Median	8.20	0.80	3.15	2.12	3.41	0.45	0.80	3.20	3.21	2.54
Skew	-1.14	-0.87	-0.02	0.83	-0.44	3.76	-0.47	-1.01	2.26	3.32

Table 4 Descriptive statistics of Zamzam groundwater heavy metals (n=29).

Sample No	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
	(µg/L)									
Maximum	7.44	0.62	72.10	0.41	1.82	3.08	0.37	7.29	0.11	0.37
Minimum	3.44	0.07	58.48	0.09	0.73	1.69	0.00	4.52	0.04	0.00
Mean	4.38	0.23	64.75	0.12	1.26	2.31	0.11	6.18	0.06	0.04
St. deviation	0.98	0.13	4.15	0.06	0.36	0.43	0.10	1.15	0.01	0.08
Variance	0.99	0.36	2.04	0.24	0.60	0.66	0.32	1.07	0.12	0.28
St. error	0.13	0.08	0.18	0.06	0.10	0.10	0.07	0.13	0.04	0.07
Median	4.26	0.23	65.64	0.11	1.06	2.19	0.09	6.93	0.06	0.00
Skew	1.67	0.91	-0.19	5.03	0.39	0.25	0.92	-0.57	1.79	3.27
WHO (2011)	50	100	300	-	20	2000	3000	10	3	10
KSA (2003)	50	200	300	-	-	2000	-	10	3	10

Table 5 Descriptive statistics of Zamzam groundwater trace elements (n=50).

Sample No	Phosphate	Nitrate	Nitrite	Bromide	Fluoride	Ammonium	Lithium
	(mg/L)						
Maximum	0.105	52.790	0.060	0.685	1.590	2.489	0.243
Minimum	0.000	30.000	0.000	0.230	0.865	0.000	0.010
Mean	0.011	35.480	0.002	0.403	0.963	0.520	0.188
St. deviation	0.032	4.478	0.011	0.070	0.125	0.740	0.062
Variance	0.179	2.116	0.106	0.265	0.354	0.860	0.249
St. error	0.054	0.185	0.041	0.065	0.076	0.118	0.063
Median	0.000	34.555	0.000	0.400	0.940	0.235	0.205
Skew	2.751	3.356	5.385	1.672	4.842	1.617	-1.929
WHO (2011)	-	50	3	-	1.5	-	-
KSA (2003)	-	50	-	-	1.5	-	-

4 Conclusions

This study delivers a comprehensive investigation of Zamzam water focused on the chemical and microbial analyses. Twenty nine water samples were collected from Mecca Almocarama inside and outside AlHaram. The available domestic Zamzam bottled waters in Mecca were also included. The distribution of chemical constituents with a focus on arsenic and nitrates were determined and compared with drinking water standards of Saudi Arabian, and World Health Organization. The results found that the dissolved salts, soluble cations and anions, Pb, Cd, As, Zn, Cu, Ni, Co, Fe, Mn, Cr, PO_4^{3-}, NO_2^-, Br^-, F^-, NH_4^+, and Li^+ are within the acceptable limits. Only 6.9% of studied samples were found to be infected by total coliform group; however, the samples collected from the main well found free of any type of microbial contamination.

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